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### (54) COATED HARD ALLOY

BESCHICHTETE HARTLEGIERUNG

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**Description****Technical Field**

5 [0001] The present invention relates to a coated hard metal material prepared by coating cemented carbide or cermet with a hard material, and more particularly, it relates to a coated hard metal material which is employed for a cutting tool. The present invention provides a cutting tool material which is excellent in wear resistance and chipping resistance, and can withstand a high-speed or high-efficiency cutting condition, in particular.

**10 Background Technique**

[0002] It is known that a cutting edge temperature of a cutting tool during cutting exceeds about 800°C at the maximum also in an ordinary cutting condition of about 100 to 300 m/min. Further in recent years, a demand for development of a tool which is cuttable under a condition of a higher speed or a higher feed rate than the conventional one, such 15 as a high speed of at least 300 m/min., for example, is increased with a car manufacturer as a leader in order to improve productivity per unit time. In consideration of the spread of NC machine tools, an effect of reducing the production cost, and the stream of shorter working hours.

[0003] However, the cutting edge temperature of the cutting tool exceeds 1000°C in such a cutting condition, and this is an extremely severe condition for the tool material. If the cutting edge temperature is increased, the cutting edge 20 is plastically deformed by heat, to cause regression of the cutting edge position. At a temperature exceeding 1000°C, further, the base material such as cemented carbide forming the tool is oxidized and wear abruptly progresses.

[0004] In order to avoid such damage of the tool by cutting, tools prepared by forming various types of hard coating 25 layers on surfaces of hard metals by chemical vapor deposition or physical vapor deposition are used. Historically, a tool coated with a Ti compound first appeared, and improvement of the cutting speed was attained since the same is superior in stability under a high temperature to cemented carbide. Thereafter a tool prepared by further coating a Ti compound with an Al<sub>2</sub>O<sub>3</sub> layer of 1 to 2 µm was developed to make it possible to further improve the cutting speed, and hence this forms the mainstream of the current coated cutting tool.

[0005] Al<sub>2</sub>O<sub>3</sub> has small standard formation free energy, and is chemically more stable than the Ti compound. Thus, it is said that an Al<sub>2</sub>O<sub>3</sub> film brings a great effect for suppression of crater wear in a cutting face portion which becomes 30 at the highest temperature in the cutting edge, and is suitable for high-speed cutting. Further, it is said that propagation of cutting heat is suppressed and a hard metal base material which is the base can be kept at a low temperature since heat conductivity of Al<sub>2</sub>O<sub>3</sub> is small. In order to develop a tool which is capable of higher speed cutting, therefore, it comes to that the Al<sub>2</sub>O<sub>3</sub> layer may be further thickened.

[0006] When the Al<sub>2</sub>O<sub>3</sub> layer is thickened, however, hardness is reduced since bulking of crystal grains forming the 35 coating layers progresses, and reduction of wear resistance on the flank comes into question. It has been recognized that, if such a tool is used in practice, the dimensions of a workpiece are changed by regression of the cutting edge position since progress of wear is quick, and the life of the tool is extremely short.

[0007] On the other hand, a method of preventing bulking of crystal grains by dividing an Al<sub>2</sub>O<sub>3</sub> layer into some layers is proposed in Japanese Patent Publication No. 5-49750. According to this method, the grain size of Al<sub>2</sub>O<sub>3</sub> can certainly 40 be reduced and wear resistance can be improved. On the other hand, boundaries between Al<sub>2</sub>O<sub>3</sub> and other materials are increased, and hence separation at the interfaces easily takes place. In cutting with a large impact such as intermittent cutting, it has been general that damage is abruptly increased due to layer separation in the flank and the cutting face, to reach the tool life.

[0008] In Japanese Patent Publication No. 6-15714, on the other hand, a coated sintered alloy prepared by coating 45 an Al<sub>2</sub>O<sub>3</sub> layer while dividing the same into an inner layer of 1 to 3 µm and an outer layer of 0.4 to 20 µm is proposed. Both of heat insulation and wear resistance are expected as the roles of the Al<sub>2</sub>O<sub>3</sub> film of the outer layer. However, the function of the outer layer as an adiabatic layer is reduced in an early stage by wear, while no specific devise is made as to wear resistance of the outer layer either. Thus, progress of wear is quick, and the life of the tool was extremely short.

[0009] A technique of employing a ZrO<sub>2</sub> film whose standard formation free energy is small similarly to Al<sub>2</sub>O<sub>3</sub> with 50 smaller heat conductivity than Al<sub>2</sub>O<sub>3</sub> is also proposed in Japanese Patent Publication No. 52-43188 or Japanese Patent Publication No. 54-34182. However, no tool employing ZrO<sub>2</sub> as a coating layer has been put into practice up to now. This is because a ZrO<sub>2</sub> layer is inferior in wear resistance since the hardness of ZrO<sub>2</sub> is low as compared with Al<sub>2</sub>O<sub>3</sub>.

[0010] Japanese Patent Publication No. 56-52109 discloses a technique of successively coating a cutting tip of cemented carbide with three layers of a lower layer, an intermediate layer and an upper layer. The lower layer is any 55 one of titanium carbide, titanium nitride and titanium carbo-nitride of 1.0 to 10.0 µm in thickness, the intermediate layer is aluminum oxide of 0.1 to 5.0 µm in thickness, and the upper layer is any one of titanium carbide, titanium nitride and titanium carbo-nitride of 0.1 to 3.0 µm in thickness. This gazette describes that the thickness of the intermediate layer must not exceed 5.0 µm since toughness is reduced if the intermediate layer exceeds 5 µm. Further, the gazette

describes that the thickness of the upper layer must not exceed 3.0  $\mu\text{m}$  since crystal grains forming the coating layers are bulked when the thickness of the upper layer exceeds 3.0  $\mu\text{m}$  and this is not preferable.

[0011] Japanese Patent Laying-Open No. 54-28316 also discloses a technique of forming coating layers of a three-layer structure on cemented carbide. The coating outermost layer consists of a nitride and/or a carbo-nitride of at least

5 any one of Ti, Zr and Hf, the intermediate layer consists of  $\text{Al}_2\text{O}_3$  and/or  $\text{ZrO}_2$ , and the coating innermost layer consists of a carbide and/or a carbo-nitride of at least any one of Ti, Zr and Hf. In its concrete example, the thickness of the innermost layer is 3  $\mu\text{m}$ , the thickness of the intermediate layer is 1  $\mu\text{m}$ , and the thickness of the outermost layer is 2  $\mu\text{m}$ . The thickness of the outermost layer is not more than the thickness of the innermost layer.

[0012] The conventional coated hard metal material having these three-layer coatings is characterized in that the same has the coating of TiN or TiCN in a thickness of not more than 3  $\mu\text{m}$  on the oxide layer. However, when a tip of such a conventional coated hard metal material is employed in high-speed cutting, particularly in such cutting that the cutting edge temperature exceeds 800°C, there have been such problems that the cutting edge of the tip is easily damaged, and dimensional change of the workpiece easily takes place. This can also be read from the description of the aforementioned gazette that the outermost layer is oxidized in high-speed/high-feed cutting and an oxide such as

15  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  is directly exposed.

#### Disclosure of the Invention

[0013] An object of the present invention is to solve the aforementioned problems, and provide a coated hard metal material which is excellent in wear resistance and chipping resistance.

[0014] Another object of the present invention is to provide a coated hard metal material for a cutting tool which can sufficiently withstand usage not only in an ordinary cutting condition but under such a strict cutting condition of a high speed or high efficiency that the cutting edge temperature exceeds 1000°C.

[0015] The present invention provides a coated hard metal material in which hard coating layers are provided on a 25 surface of a base material selected from the group consisting of cemented carbide and cermet. In the present invention, the hard coating layers comprise the following three layers:

(a) an inner layer which is formed on the base material, and consists essentially of at least one layer of a material selected from the group consisting of a carbide, a nitride, a carbo-nitride, a carbo-oxide, a carbo-nitrogen oxide 30 and a boronitride of Ti,

(b) an intermediate layer which is formed on the inner layer, and mainly composed of an oxide selected from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and a mixture or a solid solution thereof, and

(c) an outer layer which is formed on the intermediate layer, and consists essentially of at least one layer of a material selected from the group consisting of a carbide, a nitride, a carbo-nitride, a carbo-oxide, a carbonitrogen 35 oxide and a boronitride of Ti.

[0016] In the present invention, the thickness of the intermediate layer is at least 5  $\mu\text{m}$  when the same is mainly composed of  $\text{Al}_2\text{O}_3$ , and at least 0.5  $\mu\text{m}$  when the same is mainly composed of  $\text{ZrO}_2$ . The thickness of the outer layer is at least 5  $\mu\text{m}$ , and exceeds the thickness of the inner layer.

[0017] In the present invention, the thickness of the inner layer is preferably in the range of 0.1 to 5  $\mu\text{m}$ . The thickness of the intermediate layer is preferably in the range of 5 to 50  $\mu\text{m}$  when the same is mainly composed of  $\text{Al}_2\text{O}_3$ , and preferably in the range of 0.5 to 20  $\mu\text{m}$  when the same is mainly composed of  $\text{ZrO}_2$ . The thickness of the outer layer is preferably in the range of 5 to 100  $\mu\text{m}$ .

[0018] In the present invention, the outer layer is made thicker than the inner layer, and the thickness of the outer 45 layer is more largely set to be at least 5  $\mu\text{m}$ . Thus, the present invention can keep wear resistance for a longer time in cutting conditions from a low speed up to a high speed. Further, the present invention employs  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  which is excellent in heat insulation for the intermediate layer. Particularly the intermediate layer suppresses propagation of heat which is generated in the cutting edge to the base material during cutting work, and suppresses plastic deformation of the base material by heat. When deformation of the base material in cutting work is suppressed, separation of the 50 coating is also suppressed. In the present invention, at least 5  $\mu\text{m}$  is set in case of the intermediate layer which is mainly composed of  $\text{Al}_2\text{O}_3$  and at least 0.5  $\mu\text{m}$  is set in case of the intermediate layer which is mainly composed of  $\text{ZrO}_2$ , as the thickness of the intermediate layer providing sufficient heat insulation. In the present invention, the inner layer particularly contributes to adhesion of the hard coating layers to the base material. On the other hand, the intermediate layer and the outer layer particularly contribute to heat insulation and wear resistance respectively. Thus, the 55 present invention makes the three layers take charge of different functions respectively, for obtaining a coated hard metal material which can exhibit excellent performance in wide-ranging cutting conditions with this. Further, a superior one can be obtained by setting the thicknesses of the respective layers in proper ranges and/or improving adhesion between the respective layers, as described later.

## Brief Description of the Drawings

[0019] Fig. 1 is a schematic sectional view showing a concrete example of a coated hard metal according to the present invention. As shown in Fig. 1, an inner layer 2, an intermediate layer 3 and an outer layer 4 are successively formed on a base material 1.

[0020] Fig. 2A is a typical diagram showing a state of working a workpiece with a cutting tool. A workpiece 22 is worked with a cutting tool 21 which is mounted on a holder 20, and a chip 23 is caused. The cutting tool 21 is used at a clearance angle  $\theta$ . Fig. 2B is a schematic sectional view showing wear of a cutting tool. This figure shows a worn thickness D of a film 25 on a tool base material 24 in abrasion loss  $V_B$ .

[0021] Fig. 3 is a schematic sectional view showing another concrete example of the coated hard metal according to the present invention.

[0022] Fig. 4 is a schematic sectional view showing still another concrete example of the coated hard metal according to the present invention.

[0023] Fig. 5 is a schematic sectional view showing a further concrete example of the coated hard metal according to the present invention.

[0024] Fig. 6 is a schematic sectional view showing a further concrete example of the coated hard metal according to the present invention.

[0025] Fig. 7 is a schematic sectional view showing a further concrete example of the coated hard metal according to the present invention. In this material, an outer layer consists essentially of columnar crystals.

[0026] Fig. 8 is a schematic sectional view showing such a state that cracks are caused in the columnar crystals of the outer layer in the coated hard metal according to the present invention.

[0027] Fig. 9 is a schematic sectional view of a workpiece employed for a chipping resistance test of Example.

## Best Mode for Carrying Out the Invention

[0028] In the aforementioned conventional coated hard metal tool, the tool metal base material was coated with a Ti compound, and  $\text{Al}_2\text{O}_3$  of 1 to 2  $\mu\text{m}$  in thickness was coated thereon. In the prior art, further, a thin TiN or TiCN layer of not more than 3  $\mu\text{m}$  was formed on  $\text{Al}_2\text{O}_3$ . The total thickness of the coating layers was about 10  $\mu\text{m}$  in the prior art. In the prior art, further, it is conceivable that the principal role of the outermost layer consisting of TiN or TiCN is identification of a used corner by coloring, and hence the same is thinner than the film thickness of the inner Ti compound as a matter of course, so that the same is readily worn. In the conventional coated hard metal having films of a three-layer structure, therefore, the outer TiN or TiCN film is worn in an early stage, and does not contribute to wear resistance. In the prior art, those contributing to wear resistance are the inner Ti compound layer and the  $\text{Al}_2\text{O}_3$  layer.

[0029] In environment where a coated hard metal tool is used in practice, a thermocouple was embedded in a tool and the temperature of a tool portion was examined. Consequently, it has been recognized in relation to sectional temperature distribution of the tool cutting edge that the temperature of the flank was lower by about 300°C as compared with the maximum temperature of the cutting face, and the maximum temperature of the flank did not reach 1000°C also in high-speed cutting of 500 m/min. Further, wear resistance properties of a Ti compound,  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  were compared with each other at respective cutting temperatures. Consequently, it has been recognized that  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  is superior in wear resistance when the cutting temperature is at least 1000°C on the flank while the Ti compound is superior in wear resistance under such a condition that the cutting temperature of the flank is lower than 1000°C. Further, it has been proved that  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  are more effective in suppression of crater wear than the Ti compound on the cutting face at a temperature of at least 600°C.

[0030] From these facts, it comes to that the substance which is most excellent in wear resistance under such a cutting condition that the maximum temperature of the cutting face becomes about at least 600°C and not more than 1300°C, i.e., from a low speed of about 100 m/min. to a high-speed cutting condition of about 500 m/min. is  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  on the cutting face, and the Ti compound on the flank. As a coating structure in the coated hard metal, therefore, it comes to that it is preferable that only the Ti compound is coated on the flank and only  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  is coated on the cutting face. However, it is difficult to vary the deposition material with the surface in case of forming hard coating layers by vapor deposition.

[0031] In the present invention, therefore,  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  was coated on the inner side and a Ti compound was more thickly coated on the outer side, thereby improving wear resistance on the flank, to obtain a coated hard metal which can suppress dimensional change of a workpiece. As described above, the film thicknesses of the intermediate layer and the outer layer were more largely set in the coated hard metal having the inner layer consisting essentially of a Ti compound, the intermediate layer consisting essentially of  $\text{Al}_2\text{O}_3$  and/or  $\text{ZrO}_2$  and the outer layer consisting essentially of a Ti compound, to obtain that which is excellent in wear resistance and chipping resistance. When a thick Ti compound is coated on the outer side, a hard film having relatively low wear resistance can be formed inside the same. In relation to crater wear resistance, on the other hand, the oxide layer provided inside plays a role of reinforcing the outer Ti

compound layer.

[0032] In high-speed cutting, particularly at such a cutting speed that the cutting edge temperature exceeds 800°C, most problematic is plastic deformation of the base material alloy. In plastic deformation, a hard coating layer consisting of ceramics having smaller deformability than the base material cannot follow the deformation, cracks are caused in the coating layer, the cracks become larger due to cutting stress, and a workpiece is deposited thereto to readily cause separation of the layer. The prior art has not discovered a sufficient solution for this problem by plastic deformation.

[0033] As hereinabove described, further, the thickness of the outer layer is small at about 2 µm in the prior art, and hence the inner layer is readily exposed by wear. Thus, it has been difficult to suppress dimensional change of the workpiece by the flank. Although the outer layer in the prior art watches lubricity with respect to the workpiece such as steel, for example, particularly reactivity with steel on the flank, it has not aimed at improvement of wear resistance on the flank.

[0034] Further, US-A-4,357,382 discloses a cutting tool having an increased resistance to wear of the surface thereof. The tool comprises a surface coating having a first layer of one or more layers of a metallic carbide or nitride in a total thickness ranging from 0.01 to 10 µm, a second layer comprised of one or more layers of a refractory oxide in a total thickness ranging from 0.5 to 10 µm, and a third layer comprised of one or more layers of a nitride, carbonitride, oxynitride, oxycarbide or oxycarbonitride and boride of such metals as titanium, zirconium, hafnium, aluminium and silicon in a total thickness ranging from 1 to 10 µm.

[0035] US-A-4,714,660 discloses a coated cemented carbide product comprising a cemented carbide substrate and a dense chemical vapor deposited coating having a microstructure of at least two simultaneously co-deposited phases which form a composite layer. The two phases comprise (1) Ti, Zr, Hf, V, Nb or Ta (carbo)nitride, (oxy)carbide, oxycarbonitride, silicide or boride or Cr, Mo, W carbide, silicide or boride or Si or B carbide or nitride, and (2) Al, Ti, Zr, Hf, Mg, Si or Ca oxide or nitride.

[0036] It is an object of the present invention to provide a coated hard-metal material having an increased wear resistance.

[0037] This object is solved by providing a coated hard-metal material comprising the features defined and appended claim 1.

[0038] According to the present invention, on the other hand, plastic deformation of the base material can be suppressed in cutting as compared with the prior art, by employing  $Al_2O_3$  or  $ZrO_2$  which is excellent in heat insulation as the intermediate layer. Therefore, separation of the coating layers is hardly caused in a cutting tool comprising the inventive coated hard metal. Further, the same is excellent in wear resistance on the flank by making the film thickness of the outer layer of a Ti compound thicker than the inner layer and coating the same in excess of 5 µm. According to the present invention, therefore, it is possible to provide a coated hard metal cutting tool causing no dimensional change of the workpiece, which can suppress crater wear on the flank at the same time. These characteristics are brought by the intermediate layer consisting essentially of  $Al_2O_3$ ,  $ZrO_2$  or a mixture thereof having a proper thickness, and the outer layer consisting essentially of a Ti compound which is thickly formed thereon.

[0039] In the coated hard metal of the present invention, the base material is cemented carbide or cermet, i.e., a hard metal consisting essentially of an iron family metal and carbides, nitrides and carbo-nitrides of the elements of the groups IVa, Va and VIa of the periodic table. Among the hard coated layers provided on this base material, the inner layer of a Ti compound acts as a layer bonding the base material with the intermediate layer of  $Al_2O_3$  or  $ZrO_2$ , the intermediate layer of  $Al_2O_3$  or  $ZrO_2$  improves crater wear resistance and plastic deformation resistance on the cutting face, and the outer layer of a Ti compound which is coated more thickly than the inner layer contributes to improvement of wear resistance on the flank.

[0040] Therefore, a cutting tool comprising the coated hard metal of the present invention is excellent in wear resistance on the flank due to superior wear resistance of the Ti compound at not more than 1000°C, reduces dimensional change of the workpiece, and lengthens the tool life. On the cutting face portion which becomes a higher temperature than the flank portion, further, excellent crater wear resistance can be expected even if the outer layer of the Ti compound is worn, since the intermediate layer of  $Al_2O_3$  or  $ZrO_2$  is present under the same. For the tool, wear on the cutting face is not so problematic unless the base material is exposed, and wear of the outer layer of the Ti compound in an initial stage places no significant obstacle. Consequently, the cutting tool according to the present invention can exhibit excellent wear resistance in a wide-ranging condition from a low speed up to a high speed.

[0041] Among the hard coating layers, the inner layer which is formed on the base material consists essentially of at least one layer of a material selected from the group consisting of a carbide, a nitride, a carbo-nitride, a carbo-oxide, a carbonitrogen oxide and a boronitride of Ti. The reason why these Ti compounds are employed as the inner layer resides in that the same are excellent in adhesion to the hard metal which is the base material, and also excellent in adhesive property with  $Al_2O_3$  and  $ZrO_2$  being the intermediate layer. Further, its film thickness is in the range of 0.1 to 5 µm, and preferably in the range of 0.5 to 3 µm, since its effect is not attained if the thickness is less than 0.1 µm in total, while the same is too thick as an adhesion layer if the thickness exceeds 5 µm.

[0042] The intermediate layer which is formed on the inner layer is mainly composed of  $Al_2O_3$ ,  $ZrO_2$ , or a mixture or

a solid solution thereof. When the mixture is employed, either of both is contained in a large quantity as a main component. In case of an intermediate layer mainly composed of  $\text{Al}_2\text{O}_3$ , another substance, such as  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{TiO}_2$ ,  $\text{TiC}$  or  $\text{TiN}$  may be contained in a ratio of not more than 50 %, or  $\text{Ti}$ ,  $\text{Zr}$  or  $\text{Cl}$  or  $\text{N}$  may be solidly dissolved in the intermediate layer in a ratio of not more than 50 %. Further, the intermediate layer mainly composed of  $\text{Al}_2\text{O}_3$  may be divided by another film, such as a thin film of a Ti compound such as  $\text{TiC}$ ,  $\text{TiCN}$ ,  $\text{TiN}$ ,  $\text{TIBN}$ ,  $\text{TiCO}$  or  $\text{TiCNO}$ , an Al compound such as  $\text{AlN}$  or  $\text{AlNO}$ , or an oxide such as  $\text{ZrO}_2$ ,  $\text{HfO}_2$  or  $\text{TiO}_2$ , for example.

[0043] The intermediate layer mainly composed of  $\text{Al}_2\text{O}_3$  has a large effect of suppressing plastic deformation of the base material and improving crater wear resistance on the cutting face. In particular, the effect that suppression of film separation resulting from thermal deformation of the base material has been enabled by a heat insulation effect of this intermediate layer is important. However, the effect is small if its film thickness is less than 5  $\mu\text{m}$  while strength is reduced if the thickness exceeds 50  $\mu\text{m}$ , and hence the inventive range is 5 to 50  $\mu\text{m}$ , and preferable is the range of 10 to 40  $\mu\text{m}$ .

[0044] On the other hand,  $\text{ZrO}_2$  has not been put into practice since the same is low in hardness and low in wear resistance, while its heat conductivity is extremely small as compared with  $\text{Al}_2\text{O}_3$ .  $\text{Al}_2\text{O}_3$  has heat conductivity of 0.054 cal/cm $\cdot$ sec $\cdot$ °C and  $\text{ZrO}_2$  has heat conductivity of 0.005 cal/cm $\cdot$ sec $\cdot$ °C at 20°C, while  $\text{Al}_2\text{O}_3$  has heat conductivity of 0.015 cal/cm $\cdot$ sec $\cdot$ °C and  $\text{ZrO}_2$  has heat conductivity of 0.005 cal/cm $\cdot$ sec $\cdot$ °C at 1000°C. Therefore,  $\text{ZrO}_2$  is excellent in effect of suppressing plastic deformation of the base material, and a heat insulation effect substantially identical to that of  $\text{Al}_2\text{O}_3$  is attained in a layer which is thinner than  $\text{Al}_2\text{O}_3$ .

[0045] Based on such recognition, a tool prepared by providing an intermediate layer of  $\text{ZrO}_2$  on the thin inner layer of a Ti compound which was formed on a base material and coating a thick outer layer of a Ti compound thereon was produced by way of trial, and a high-speed cutting test was executed. Consequently, it has been recognized that the tool having the coating structure of the present invention is superior in plastic deformation and superior in wear resistance on the flank as compared with a tool having the conventional coating structure. It has been proved that dimensional change of a workpiece is hardly caused and crater wear on the cutting face can also be suppressed at the same time when cutting is performed by employing the tool according to the present invention.

[0046] Further, it has also been proved that, also as compared with case of employing  $\text{Al}_2\text{O}_3$  for the intermediate layer, the  $\text{ZrO}_2$  intermediate layer can not only attain excellent plastic deformation resistance with a thinner film but the film thickness can be reduced, whereby smoothness of the coating surface is improved and separation resistance is improved. To our surprise, further, such an unexpected effect has been attained that boundary wear coming into question in cutting of a readily work-hardened workpiece such as stainless is reduced and chipping resistance is improved. Although the reason therefor is not clear, this is conceivably because the Young's modulus of  $\text{ZrO}_2$  is small and its hardness is low and hence its deformability is large.

[0047] In case of employing the intermediate mainly composed of  $\text{ZrO}_2$ , another oxide such as  $\text{Al}_2\text{O}_3$ ,  $\text{HfO}_2$  or  $\text{TiO}_2$ , for example,  $\text{TiC}$  or  $\text{TiN}$  may be contained in a ratio of not more than 50 %, or  $\text{Al}$ ,  $\text{Ti}$ ,  $\text{Cl}$  or  $\text{N}$  may be solidly dissolved in the intermediate layer in a ratio of not more than 50 %. Further, the intermediate layer mainly composed of  $\text{ZrO}_2$  may be divided by another film, such as a thin film of a Ti compound such as  $\text{TiC}$ ,  $\text{TiCN}$ ,  $\text{TiN}$ ,  $\text{TIBN}$ ,  $\text{TiCO}$  or  $\text{TiCNO}$ , a Zr compound such as  $\text{ZrN}$  or  $\text{ZrC}$ , or an oxide such as  $\text{Al}_2\text{O}_3$ ,  $\text{HfO}_2$  or  $\text{TiO}_2$ , for example. The intermediate layer mainly composed of  $\text{ZnO}_2$  has a large effect of suppressing plastic deformation of the base material and improving crater wear resistance on the cutting face. In particular, such an effect that suppression of film separation resulting from deformation of the base material has been enabled by this intermediate layer is important. However, the effect is small if its film thickness is less than 0.5  $\mu\text{m}$  while strength is reduced if the thickness exceeds 20  $\mu\text{m}$ , and hence the inventive range is 0.5 to 20  $\mu\text{m}$ , and preferable is the range of 3 to 15  $\mu\text{m}$ .

[0048] The outer layer which is formed on the intermediate layer consists essentially of at least one layer of a material selected from the group consisting of a carbide, a nitride, a carbo-nitride, a carbo-oxide, a carbonitrogen oxide and a boronitride of  $\text{Ti}$ , and effectively improves wear resistance on the flank. The reason why the film thickness of the outer layer is set to be at least 5  $\mu\text{m}$  is now described. When the inventors collected used tools in a steel part working line of a car manufacturer and investigated damaged states of the tools, they confirmed that almost all the tools exhibited flank wear of at least 0.05 mm. A cutting tool is used at a clearance angle  $\theta$  of 5 to 6° as shown in Fig. 2A, and hence abrasion  $V_B$  of 0.05 mm corresponds to that a film of about 5  $\mu\text{m}$  (0.05 mm  $\times$   $\tan\theta$ ) is worn at the maximum, as shown in Fig. 2B. Therefore, the lower layer or the base material which is inferior in wear resistance is exposed and the tool tends to have a short life unless a film of at least 5  $\mu\text{m}$  which is excellent in wear resistance is provided on the tool surface. Therefore, it is necessary to employ a Ti compound film exhibiting excellent wear resistance at 100 m/min. to 500 m/min. as the outer layer and to coat the same in excess of 5  $\mu\text{m}$ . However, strength is reduced if 100  $\mu\text{m}$  is exceeded, and hence the film thickness is preferably in the range of 5 to 100  $\mu\text{m}$ . In such a cutting condition that the cutting speed exceeds 300 m/min., a film thickness of at least 10  $\mu\text{m}$  is particularly preferable, and the range of 15 to 50  $\mu\text{m}$  is more preferable.

[0049] In case of employing the intermediate layer mainly composed of  $\text{Al}_2\text{O}_3$ , the total of the film thicknesses of the hard coating layers is preferably in the range of 25 to 60  $\mu\text{m}$ . In this range, it is possible to more effectively protect the

base material, and to attain further excellent chipping resistance. In case of the intermediate layer mainly composed of  $ZrO_2$ , on the other hand, the total of the film thicknesses of the hard coating layers is preferably in the range of 20 to 60  $\mu m$ . In this range, the base material is more effectively protected, and more excellent chipping resistance is attained.

5 [0050] It has been proved that, in case of directly coating a Ti compound on the intermediate layer of  $Al_2O_3$ , it is difficult to make the film thickness of the outer Ti compound larger since adhesion between both is low. In the present invention, it is preferable to further provide a thin film between the intermediate layer of  $Al_2O_3$  and the outer layer. This film is formed in direct contact with the intermediate layer, and a film thickness of 0.1 to 2  $\mu m$  is preferable. This thin film can be brought into an Al-containing thin film consisting essentially of a material which is selected from the group 10 consisting of a nitride and an oxy-nitride of Al. In case of employing such an Al-containing thin film, it is more preferable that the nitrogen content in the thin film is reduced as the film approaches the intermediate layer, and the oxygen content is increased as the film approaches the intermediate layer. This thin film improves the adhesion between the  $Al_2O_3$  intermediate layer and the outer layer of the Ti compound. Due to this thin film, separation between the layers 15 hardly takes place, and excellent wear resistance is attained. In particular, the adhesion between the intermediate layer and the outer layer is further increased by continuously changing the composition of the thin film between  $Al_2O_3$  and AlN or AlON as described above, so that separation more hardly takes place.

15 [0051] In case of the intermediate layer mainly composed of  $ZrO_2$ , on the other hand, it is preferable to further form a Zr-containing thin film consisting essentially of a material which is selected from the group consisting of a carbide, a nitride, a carbo-nitride, a carbo-oxide, an oxy-nitride and a carbonitrogen oxide of Zr between the intermediate layer 20 and the outer layer in contact with the intermediate layer. The thickness of this thin film is preferably 0.1 to 2  $\mu m$ . Due to this thin film, adhesion between the intermediate layer and the outer layer is increased, and a thicker outer layer can be formed. Due to excellent adhesion, further, separation between the layers hardly takes place, and excellent wear resistance can be attained. Also in this case, it is preferable that the nitrogen content and/or the carbon content 25 is reduced as the film approaches the intermediate layer and the oxygen content is increased as the film approaches the intermediate layer, in the Zr-containing thin film. Thus, more excellent adhesion is attained and separation of the layers can be more effectively suppressed, by continuously changing the composition between  $ZrO_2$  and the Zr compound.

25 [0052] A structure of further forming a thin film between an intermediate layer and an outer layer is shown in Fig. 3. Referring to Fig. 3, an inner layer 2 is formed on a base material 1, and an intermediate layer 3 is formed thereon. The 30 intermediate layer 3 is tightly bonded to an outer layer 4 through an Al- or Zr-containing thin film 10.

30 [0053] As shown in Fig. 4, on the other hand, a thin film may be further formed between an intermediate layer 3 and an outer layer 4, in addition to the Al- or Zr-containing thin film. In such a coating, therefore, the inner layer 2 is formed on the base material 1, and the intermediate layer 3 is formed thereon. The Al- or Zr-containing thin film 10 is formed on the intermediate layer 3. The Al- or Zr-containing thin film 10 is tightly bonded to the outer layer 4 through a thin 35 film 12. Such a thin film 12 can be made of a material selected from the group consisting of TiBNO, TiNO and  $TiO_2$ .

35 [0054] On the other hand, a thin film consisting essentially of a material which is selected from the group consisting of TiBN, TiCO and TiCNO can be employed in place of the Al- or Zr-containing layer, in order to improve adhesion between the intermediate layer and the outer layer. Such a thin film belongs the outer layer defined in the above. A structure employing this thin film is shown in Fig. 5. The inner layer 2 is formed on the base material 1, and the intermediate layer 3 is formed thereon. The intermediate layer 3 is tightly bonded to the outer layer 4 through a thin film 14 40 consisting essentially of TiBN, TiCO or TiCNO. Stronger adhesion is attained by employing such a material for a portion of the outer layer which comes into contact with the intermediate layer.

40 [0055] It is also possible to provide a thin film consisting essentially of a material which is selected from the group 45 consisting of TiBNO, TiNO and  $TiO_2$  between the intermediate layer and the outer layer, in contact with the intermediate layer. A structure employing such a thin film is shown in Fig. 6. The inner layer 2 is formed on the base material 1, and the intermediate layer 3 is formed thereon. The intermediate layer 3 is tightly bonded to the outer layer 4 through a thin film 16. The thin film 16 can be brought into a thin film of TiBNO, TiNO, or  $TiO_2$ . The thickness of this film is preferably in the range of 0.1 to 2  $\mu m$ .

45 [0056] For improving the chipping resistance the outer layer according to the invention is mainly of columnar crystals. 50 When hard coating layers are deposited on the base material by chemical vapor deposition or the like, tensile residual stress is caused on the coating layers due to the difference between the thermal expansion coefficients of the base material and the coating layers and hence chipping resistance of the tool is generally reduced. However, it has been presumed that, when the outer layer 4 is mainly of columnar crystals 5 as shown in Fig. 7, tensile residual stress is readily released in such a form that cracks 6 are caused in grain boundaries of the columnar crystals 5, to hardly cause 55 large chipping reaching the tool life.

55 [0057] Therefore, it is possible to increase the film thickness of the outer layer 4 by making the outer layer 4 of the columnar crystals 5 in the inventive coated hard metal providing an inner layer 2 of a Ti compound on a base material 1, providing the intermediate layer 3 mainly composed of  $Al_2O_3$  or  $ZrO_2$  thereon, and providing the outer layer 4 of a

Ti compound further thereon as shown in Fig. 7, so that further excellent wear resistance can be exhibited over a long period.

[0058] When the aspect ratio of the columnar crystals 5 is 5 to 80, improvement of wear resistance and chipping resistance is particularly remarkable. Here, the aspect ratio is the ratio  $l/d$  of the length  $l$  of the columnar crystals 5 to the crystal grain diameter  $d$ , as shown in Fig. 7. Its measurement was performed by photographing a section of the hard coating layer by TEM, and obtaining an average value of arbitrary three visual fields.

[0059] Particularly when the outer layer consists essentially of TiCN of columnar crystals, wear resistance on the flank and chipping resistance are more excellent. Above all, particularly excellent wear resistance is attained when the C:N ratio of TiCN is in the range of 5:5 to 7:3 in molar ratio. This is because hardness and toughness of the coating layer is well-balanced to exhibit excellent wear resistance and chipping resistance when the C:N ratio of TiCN is in this range. The molar ratio of the C:N ratio can be measured by obtaining the lattice constant of the TiCN outer layer by analysis through ESCA (ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS) or EPMA (ELECTRON PROBE MICRO ANALYSIS), or X-ray analysis.

[0060] According to a result obtained by the inventors through X-ray analysis, the lattice constant of TiCN having a molar ratio of the C:N ratio within the range of 5:5 to 7:3 was in the range of 4.275 to 4.295, and particularly excellent wear resistance and chipping resistance were exhibited at this time. While this result includes deviation in consideration of TiCN of a stoichiometric composition, it seems that such deviation has been caused since TiCN may have a non-stoichiometric composition such as  $Ti(CN)_{0.9}$ , for example.

[0061] Further, TiCN of the outer layer preferably has maximum peak strength of X-ray diffraction, as to a crystal plane selected from the group consisting of (111), (422) and (311). A TiCN film of the outer layer exhibiting such characteristics is excellent in adhesion with the lower layer.

[0062] In the hard coating layers, the thickest layer which is included in the inner layer preferably consists essentially of a layer mainly composed of columnar crystals having an aspect ratio of 5 to 30. Such an inner layer can have high strength. When the aspect ratio is set in this range in case of thickening the inner layer, strength reduction of the inner layer can be suppressed.

[0063] On the other hand, the intermediate layer preferably includes a layer mainly composed of columnar crystals having an aspect ratio of 3 to 20. The strength and toughness of the intermediate layer do not depend on the grain size alone, but also depends on the aspect ratio of the crystal grains. The inventors have discovered that the strength and toughness can be improved by making the aspect ratio of the crystal grains in the intermediate layer 3 to 20. Further, the inventors have discovered that the degree of bulking of the crystal grains is small and the aspect ratio of the crystal grains can be increased even if the film of  $Al_2O_3$  or  $ZrO_2$  is thickened. And it has been proved that a film which is excellent in strength and toughness can rather be obtained by thickening the film.

[0064] It is more preferable that  $Al_2O_3$  of the intermediate layer is mainly composed of  $\alpha$ - $Al_2O_3$ . A crystal grain having an aspect ratio of 3 to 20 can be readily formed by making the crystal system of  $Al_2O_3$  an  $\alpha$  type, and a film which is excellent in strength and toughness can be obtained. Further, the  $\alpha$ - $Al_2O_3$  film preferably has the maximum peak strength of X-ray diffraction as to a crystal plane which is selected from the group consisting of (104) and (116). Thus, adhesion between the outer layer and the  $Al_2O_3$  film can be improved.

[0065] On the other hand, the crystal system of  $Al_2O_3$  in the intermediate layer can be mainly composed of  $\kappa$ - $Al_2O_3$  around a portion which is in contact with the inner layer and around a portion which is in contact with the outer layer. The adhesion between the inner and outer layers and the intermediate layer can be improved by providing  $\kappa$ - $Al_2O_3$  in the portions which are in contact with the outer layer and the inner layer respectively. Further, an intermediate layer which is excellent in strength and toughness and excellent in adhesion can be obtained by forming an intermediate layer holding  $\alpha$ - $Al_2O_3$  with  $\kappa$ - $Al_2O_3$ .

[0066] The inventors have discovered that particularly excellent separation resistance and chipping resistance can be provided by controlling the distances between cracks which are formed on the hard coating layers at proper values. Namely, the average of the distances between adjacent cracks is preferably 20 to 40  $\mu m$ , in relation to a plurality of cracks which are formed on the hard coating layers. Further, the distances between cracks in the inner layer and the outer layer are preferably smaller than those between cracks in the intermediate layer. Excellent chipping resistance and wear resistance can be attained by thus controlling the distribution state of the cracks. Particularly in a coating having a thickness of at least 25  $\mu m$ , the effect of controlling the distances between the cracks in this range is remarkable. Due to such control of the distances between the cracks, employment of a coated hard metal having thicker films which was generally regarded as unemployable has been enabled.

[0067] The inner layer, the intermediate layer and the outer layer according to the present invention can be formed by ordinary chemical vapor deposition or physical vapor deposition. In case of forming the outer layer of TiCN on the intermediate layer of  $Al_2O_3$  or  $ZrO_2$  by chemical vapor deposition, TiCN can be coated at 700 to 1100°C with pressure of not more than 500 Torr while employing  $TiCl_4$  as a Ti source of raw material gas, an organic carbo-nitride as a carbon and nitrogen source, and hydrogen gas as carrier gas. According to such a step, homogeneous and fine nucleation of TiCN is performed on  $Al_2O_3$  or  $ZrO_2$ , whereby a hard coating layer which is excellent in adhesion with the intermediate

layer, hardly causes interlayer separation, and exhibits excellent wear resistance can be obtained.

[0068] When an organic carbo-nitride such as CH<sub>3</sub>CN, for example, is employed as a carbon and nitrogen source in the aforementioned method, in particular, the crystal grains of the TiCN outer layer can be readily brought into columnar crystals, it is easy to increase the aspect ratio of the columnar crystals, and the TiCN outer layer having a 5 molar ratio of the C:N ratio within the range of 5:5 to 7:3 can be readily formed.

[0069] In the coated hard metal of the present invention, further, a film of an oxide which is selected from the group consisting of Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and HfO<sub>2</sub> can be coated on the outer layer in a thickness of 0.5 to 5 μm in total. Boundary wear and deterioration of the Ti compound film in portions other than a worn portion can be prevented by covering the outer layer with such a film. Particularly an effect of suppressing boundary wear was remarkable in cutting of an un-10 cuttable material such as stainless steel. The effect is small if the thickness of this film is smaller than 0.5 μm, and wear resistance on the flank is reduced if the same is larger than 5 μm. In particular, the range of the thickness is preferably 1 to 3 μm. Further, this film is preferably thinner than the intermediate layer. A thin film of TiN or ZrN exhibiting a golden color may be coated on the outermost surface of the coated hard metal of the present invention. This is because these golden colors are useful for identification of used corners.

[0070] The coated hard metal of the present invention can be employed for a cutting tool. Therefore, the coated hard metal of the present invention can have the shape of a cutting tool such as a tip, for example. In the cutting edge of a cutting tool which is formed by the coated hard metal of the present invention, it is more preferable that parts of the hard coating layers are removed, and a surface whose average value of surface roughness Ra is not more than 0.05 15 μm is formed. A cutting tool which is excellent in wear resistance can be provided by forming such a smooth surface 20 on a portion of the cutting edge.

[0071] While embodiments of the present invention are now shown in Examples, the present invention is not restricted by these Examples.

#### Example 1

[0072] ISO M20 cemented carbide (base material 1), ISO K20 (base material 2) and a commercially available cermet tool (base material 3) were prepared as base materials, and any one of hard coating layers shown in Table 1 was 25 formed on each base material by well-known chemical vapor deposition at a deposition temperature of 1000°C, to prepare tip-shaped tools of SNGN120408 respectively.

[Table 1]

Symbol	Structure of Hard Coating Layer (left side = base material side, inside parenthesis = film thickness(μm))
A	TiN(0.5)/Al <sub>2</sub> O <sub>3</sub> (10)/TiCN(15)
B	TiC(0.5)/TiCN(3)/TiBN(0.5)/Al <sub>2</sub> O <sub>3</sub> (5)/TiN(7)
C	TiCN(2)/TiCO(0.5)/Al <sub>2</sub> O <sub>3</sub> (20)/TiCN(20)
D	TiN(0.5)/TiCNO(0.5)/Al <sub>2</sub> O <sub>3</sub> (45)/TiCN(30)/TiC(10)
E	Al <sub>2</sub> O <sub>3</sub> (10)/TiCN(15)
F	TiN(0.5)/Al <sub>2</sub> O <sub>3</sub> (2)/TiCN(15)
G	TiN(0.5)/TiCN(15)/Al <sub>2</sub> O <sub>3</sub> (10)
H	TiN(0.5)/Al <sub>2</sub> O <sub>3</sub> (10)
I	TiN(1)/TiBN(0.5)/Al <sub>2</sub> O <sub>3</sub> (10)/TiC(0.5)/TiCN(10)

(Note) In relation to the structures of the hard coating layers in Table, the fact that the left sides are base material sides and the interiors of the parentheses indicate film thicknesses (μm) also applies to the following Tables.

[0073] The respective tips forming the hard coating layers on the base materials were employed for cutting work-pieces of SCM415 under cutting conditions of the following Table 2, and cutting performance was evaluated. The results 50 are shown in Table 3, along with the combinations of the base materials and the hard coating layers.

[Table 2]

Cutting Condition	Cutting Speed (m/min)	Feed Rate (mm/rev)	Depth of Cut (mm)	Cutting Oil	Holder	Life Criterion
1	500	0.5	1.5	no	FN11R44A	$V_B=0.15\text{mm}$
2	200	0.4	1.5	yes	FN11R44A	$V_B=0.15\text{mm}$
3	100	0.3	1.5	no	FN11R44A	chipping

10

[Table 3]

Sample	Base Material	Coating Layer	Cutting Performance	
			Cutting Condition 1	Cutting Condition 2
1	1	A	5min. 11sec.	102min. 17sec.
2	2	B	4min. 23sec.	61min. 27sec.
3	3	C	9min. 8sec.	89min. 46sec.
4	1	D	18min. 39sec.	73min. 51sec.
5*	1	E	separated in 19sec.	separated in 2min. 14sec.
6*	1	F	chipped in 45min.	87min. 35sec.
7*	1	G	1min. 56sec.	29min. 7sec.
8*	1	H	2min. 4sec.	16min. 29sec.

(Note) Samples provided with \* in Tables are comparative examples (and so forth).

30 [0074] From the above results, it is understood that the tips of the samples 1 to 4 of Inventive Example exhibit excellent cutting performance not only in high-speed cutting (cutting conditions 1) but low-speed cutting (cutting conditions 2). By comparison of the samples 1 and 5, an effect of having a Ti compound as an inner layer is understood. From comparison of the samples 1 and 6, it is understood that the effect is small if the film thickness of the  $\text{Al}_2\text{O}_3$  intermediate layer is 2  $\mu\text{m}$ , while it is understood by comparison of the samples 1 and 7 that  $\text{Al}_2\text{O}_3$  is superior in wear resistance when the same is employed as an intermediate layer rather than being coated as an outer layer. By comparison of the samples 1 and 8, it is understood that the Ti compound is superior in wear resistance to  $\text{Al}_2\text{O}_3$  as an outer layer.

#### Example 2

40 [0075] Hard coating layers shown in the following Table 4 were formed on surfaces of the base materials 1 in the above Example 1, to prepare tips of samples 9 to 14. These tips were employed for evaluating cutting performance by the cutting conditions 2 similarly to Example 1. A workpiece 7 consisting of SCM435 having four grooves 8 on its circumference as shown in Fig. 9 was employed for testing chipping resistance by the cutting conditions 3 of the above Table 2. The chipping resistance was evaluated by cutting times up to chipping of the tips. These results are shown in Table 4 together.

45

[Table 4]

Sample	Structure of Hard Coating Layer	Wear Resistance		Chipping Resistance
		Cutting Condition 2	Cutting Condition 3	
9*	$\text{Al}_2\text{O}_3(10)/\text{TiCN}(15)$	Separated in 1min 38sec.	2min. 50sec.	
10	$\text{TiC}(0.2)/\text{Al}_2\text{O}_3(10)/\text{TiCN}(15)$	65min.51sec.	4min. 29sec.	
11	$\text{TiC}(0.5)/\text{Al}_2\text{O}_3(10)/\text{TiCN}(15)$	89min. 33sec.	5min. 41sec.	
12	$\text{TiC}(3)/\text{Al}_2\text{O}_3(10)/\text{TiCN}(15)$	115min. 45sec.	5min. 12sec.	
13	$\text{TiC}(5)/\text{Al}_2\text{O}_3(10)/\text{TiCN}(15)$	93min. 29sec.	4min. 44sec.	
14*	$\text{TiC}(10)/\text{Al}_2\text{O}_3(10)/\text{TiCN}(15)$	87min. 47sec.	3min. 47sec.	

[0076] As understood from the above results, the sample 9 having no Ti compound as an inner layer caused separation of the coating layers in an early stage in a wear resistance test since adhesion of the coating layers was low, and was of an extremely short life. The tip of the sample 14 exhibited a result slightly short of chipping resistance since the film thickness of the inner layer was large, while the same is excellent as to wear resistance. On the other hand, the samples 10 to 13 of inventive Example are excellent in wear resistance and chipping resistance, while the samples 11 and 12 are excellent in balance between wear resistance and chipping resistance in particular.

## 5 Example 3

[0077] Hard coating layers shown in the following Table 5 were formed on surfaces of the base materials 2 in the above Example 1, to prepare tips of samples 15 to 21. These tips were employed for evaluating cutting performance by the cutting conditions 1 similarly to Example 1. Similarly to Example 2, further, chipping resistance was tested by the cutting conditions 3. These results are shown in Table 5 together.

15 [Table 5]

Sample	Structure of Hard Coating Layer	Wear Resistance	Chipping Resistance
		Cutting Condition 1	Cutting Condition 2
15*	TiCN(2)/Al <sub>2</sub> O <sub>3</sub> (0.5)/TiC(13)	Chipped in 1min. 13sec.	6min. 52sec.
16	TiCN(2)/Al <sub>2</sub> O <sub>3</sub> (5)/TiC(13)	9min. 51sec.	7min. 24sec.
17	TiCN(2)/Al <sub>2</sub> O <sub>3</sub> (10)/TiC(13)	12min. 3sec.	7min. 33sec.
18	TiCN(2)/Al <sub>2</sub> O <sub>3</sub> (20)/TiC(13)	12min. 54sec.	6min. 53sec.
19	TiCN(2)/Al <sub>2</sub> O <sub>3</sub> (38)/TiC(13)	12min. 29sec.	5min. 47sec.
20	TiCN(2)/Al <sub>2</sub> O <sub>3</sub> (48)/TiC(13)	10min. 47sec.	3min. 51sec.
21*	TiCN(2)/Al <sub>2</sub> O <sub>3</sub> (60)/TiC(13)	10min. 21sec.	2min. 28sec.

[0078] As understood from the above results, the samples other than the sample 15 having a small film thickness of the intermediate layer of Al<sub>2</sub>O<sub>3</sub> and the sample 21 having a large thickness exhibited cutting performance which is excellent in balance between wear resistance and chipping resistance, and the tips of the samples 17, 18 and 19 exhibited particularly excellent cutting performance above all.

## 35 Example 4

[0079] Hard coating layers shown in the following Table 6 were formed on surfaces of the base materials 3 in the above Example 1, to prepare tips of samples 22 to 28. These tips were employed for evaluating cutting performance by the cutting conditions 1 and 2 similarly to Example 1, and chipping performance was tested by the cutting conditions 3 similarly to Example 2. These results are shown in Table 6 together.

40 [Table 6]

Sample	Structure of Hard Coating Layer	Wear Resistance	Wear Resistance	Chipping Resistance
		Cutting Condition 1	Cutting Condition 2	Cutting Condition 3
22*	TiN(4)/Al <sub>2</sub> O <sub>3</sub> (10)/TiCN(2)	chipped in 3min. 5sec.	chipped in 18min. 3sec.	8min. 2sec.
23	TiN(4)/Al <sub>2</sub> O <sub>3</sub> (10)/TiCN (10)	7min. 24sec.	25min. 14sec	7min. 15sec.
24	TiN(4)/Al <sub>2</sub> O <sub>3</sub> (10)/TiCN (15)	9min. 28sec.	55min. 21sec.	6min. 39sec.
25	TiN(4)/Al <sub>2</sub> O <sub>3</sub> (10)/TiCN (30)	10min. 31sec.	84min. 53sec.	5min. 56sec.
26	TiN(4)/Al <sub>2</sub> O <sub>3</sub> (10)/TiCN (46)	11min. 23sec.	74min. 31sec.	5min. 12sec.

[Table 6] (continued)

5	Sample	Structure of Hard Coating Layer	Wear Resistance	Wear Resistance	Chipping Resistance
			Cutting Condition 1	Cutting Condition 2	Cutting Condition 3
27	27	TiN(4)/Al <sub>2</sub> O <sub>3</sub> (10)/TiCN (95)	10min. 19sec.	63min. 16sec.	3min. 4sec.
10	28*	TiN(4)/Al <sub>2</sub> O <sub>3</sub> (10)/TiCN (120)	6min. 5sec.	52min. 47sec.	1min. 57sec.

[0080] As understood from the above results, the samples other than the sample 22 having a small film thickness of the outer layer of TiCN and the sample 28 having a large thickness exhibited cutting performance which is excellent in balance between wear resistance and chipping resistance, and the tips of the samples 24, 25 and 26 exhibited particularly excellent cutting performance above all.

[0081] From the results shown in Table 5 of the above Example 3 and Table 6 of Example 4, it is understood that the samples 16 to 19 and 24 to 26 in which total film thicknesses of the hard coating layers are within the range of 25 to 60 µm are particularly excellent in balance between wear resistance and chipping resistance.

#### 20 Example 5

[0082] Hard coating layers consisting of the structure of symbol I in the above Table 1 were formed on surfaces of the base materials 1 in the above Example 1, to prepare tips of samples 29 to 34. The shapes of crystal grains of TiCN layers of the outermost sides in these samples were varied by changing film forming conditions. These tips were employed for evaluating cutting performance by the cutting conditions 2 similarly to Example 1, and chipping performance was tested by the cutting conditions 3 similarly to Example 2. These results are shown in Table 7 together.

[Table 7]

30	Sample	Aspect Ratio of TiCN Layer	Wear Resistance	Chipping Resistance
			Cutting Condition 2	Cutting Condition 3
29*	29*	1.5	51min. 13sec.	3min. 25sec.
30	30	5	70min. 32sec.	5min. 16sec.
35	31	15	79min. 45sec.	7min. 4sec.
32	32	35	85min. 11sec.	8min. 21sec.
33	33	70	78min. 7sec.	7min. 36sec.
40	34*	100	62min. 24sec.	7min. 54sec.

(Note) Samples provided with \* are comparative examples.

[0083] It is understood that the samples are excellent in wear resistance and chipping resistance when the aspect ratios of TiCN forming the TiCN layers on the outermost sides among the outer coating layers are within the range of 5 to 80, and the samples 31 and 32 exhibit particularly excellent performance above all.

#### Example 6

[0084] When the C:N ratio of the TiCN layer which is the outer layer of the tip of the sample 1 (base material 1, hard coating layer A) prepared in the above Example 1 was calculated by obtaining the lattice constant through X-ray diffraction, it was 4:6 in molar ratio. Then, TiCN layers having different C:N ratios shown in Table 8 were formed as outer layers by varying flow ratios of raw material gas while inner layers and intermediate layers were identical to the sample 1, thereby preparing tips of samples 35 to 38.

[0085] These tips were employed for evaluating cutting performance by the cutting conditions 1 and 2 similarly to Example 1, and chipping resistance was tested by the cutting conditions 3 similarly to Example 2. These results are shown in Table 8 together.

[Table 8]

Sample	C:N Ratio of TiCN Layer	Wear Resistance	Wear Resistance	Wear Resistance
		Cutting Condition 1	Cutting Condition 2	Cutting Condition 3
1	4:6	5min. 11sec.	102min. 17sec.	5min. 22sec.
35	5:5	7min. 23sec.	124min. 32sec.	6min. 13sec.
36	6:4	8min. 54sec.	141min. 8sec.	5min. 54sec.
37	7:3	7min. 42sec.	149min. 44sec.	4min. 57sec.
38	8:2	7min. 21sec.	137min. 51sec.	3min. 42sec.

[0086] From the above results, it is understood that the tips of the samples 35 to 37 whose C:N ratios are within the range of 5:5 to 7:3 in molar ratio are excellent in wear resistance and chipping resistance, and exhibit excellent cutting performance.

#### Example 7

[0087] In case of forming the hard coating layers of symbol D of the above Table 1 on the surface of the base material 1, formation of the TiCN layer among the outer layer was performed by employing  $TiCl_4$  and  $CH_3CN$  as raw material gas and hydrogen gas as carrier gas under  $1000^\circ C$  and pressure of 50 Torr, thereby preparing a tip of a sample 39. Table 9 shows results of employing the obtained tip and evaluating cutting performance by the cutting conditions 1 and 2.

[0088] Further, Table 9 also shows results of similar evaluation as to the sample 4 prepared by forming a TiCN layer by ordinary CVD similarly to the above except that  $TiCl_4$ ,  $CH_4$  and nitrogen gas were employed as raw material gas and hydrogen gas was employed as carrier gas. From Table 9, it is understood that the sample 39 employing  $CH_3CN$  as raw material gas exhibits superior cutting performance.

[Table 9]

Sample	Wear Resistance	Wear Resistance
	Cutting Condition 1	Cutting Condition 2
4	18min. 39sec.	75min. 51sec.
39	24min. 51sec.	103min. 14sec.

#### Example 8

[0089] In the tip of the sample 11 of the above Example 2, tips of samples 40 to 45 forming thin films consisting of  $TiBN$ ,  $TiBNO$ ,  $TiNO$ ,  $TiCO$ ,  $TiCNO$ , or  $TiO_2$  between intermediate layers of  $Al_2O_3$  and outer layers of TiCN by ordinary CVD at  $1000^\circ$  in film thicknesses of about  $0.5 \mu m$  were prepared. As raw material gas,  $TiCl_4$ ,  $CH_4$ ,  $N_2$ ,  $H_2$ ,  $CO$ ,  $NH_3$  and  $BCl_3$  were used in response to the film qualities. Results of evaluating wear resistance and chipping resistance as to the obtained respective tips are shown in Table 10 in comparison with the tip of the sample 11.

[Table 10]

Sample	Thin Film	Wear Resistance	Chipping Resistance
		Cutting Condition 2	Cutting Condition 3
11	no	89min. 33sec	5min. 41sec.
40	$TiBN$	131min. 17sec.	7min. 15sec.
41	$TiBNO$	125min. 23sec.	7min. 4sec.
42	$TiNO$	108min. 5sec.	6min. 35sec.
43	$TiCO$	133min. 41sec.	6min. 52sec.
44	$TiCNO$	147min. 59sec.	7min. 29sec.
45	$TiO_2$	102min. 31sec.	6min. 19sec.

[0090] From the results, it is understood that the samples 40 to 45 forming the thin films consisting of TiBN, TiBNO, TiNO, TiCO, TiCNO, or  $TiO_2$  between the intermediate layers of  $Al_2O_3$  and the outer layers of TiCN exhibit superior cutting performance to the sample 11 not provided with these thin films.

5 Example 9

[0091] In the tip of the sample 25 of the above Example 4, tips of samples 46 to 47 forming thin films consisting of AlN or AION between intermediate layers of  $Al_2O_3$  and outer layers of TiCN by ordinary CVD at 1000°C in film thicknesses of about 0.5  $\mu m$  were prepared. As to raw material gas,  $AlCl_4$ ,  $CO_2$ ,  $N_2$  and  $H_2$  were used in response to the film qualities. Results of evaluating wear resistance and chipping resistance as to the obtained respective tips are shown in Table 11 in comparison with the tip of the sample 25.

[Table 11]

15	Sample	Thin Film	Wear Resistance	Chipping Resistance
			Cutting Condition 2	Cutting Condition 3
20	25	none	84min. 54sec.	5min. 56sec.
	46	AlN	145min. 21sec.	7min. 19sec.
	47	AION	151min. 39sec.	7min. 2sec.

[0092] From the above results, it is understood that the samples 46 to 47 forming the thin films consisting of AlN or AION between the intermediate layers of  $Al_2O_3$  and the outer layers of TiCN exhibit excellent cutting performance as compared with the sample 25 not provided with these thin films.

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## Example 10

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[0093] In the tip of the sample 25 of the above Example 4, samples 46-c and 47-c forming layers whose compositions were continuously changed from  $Al_2O_3$  to AlN, or from  $Al_2O_3$  to AION between intermediate layers of  $Al_2O_3$  and outer layers of TiCN in film thicknesses of about 0.5  $\mu m$  were prepared. These layers were prepared by employing ordinary CVD and continuously reducing raw material gas ratios of  $CO_2/N_2$  while continuously changing the temperatures from 900°C to 1000°C. Results of employing the obtained tips and evaluating wear resistance and chipping resistance are shown in Table 12, in comparison with the samples 46 and 47 whose compositions are not continuously changed.

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[Table 12]

40	Sample	Thin Film	Wear Resistance	Chipping Resistance
			Cutting Condition 2	Cutting Condition 3
45	46	AlN	145min. 21sec.	7min. 19sec.
	47	AION	181min. 39sec.	7min. 2sec.
	46-c	$Al_2O_3$ -AlN	183min. 13sec.	8min. 14sec.
	47-c	$Al_2O_3$ -AION	186min. 11sec.	8min. 9sec.

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[0094] From the above results, it is understood that the samples 46-c and 47-c in which the compositions of the thin films were continuously changed in relation to the samples forming the thin films consisting of AlN or AION between the intermediate layers of  $Al_2O_3$  and the outer layers of TiCN exhibit further superior cutting performance as compared with the samples 46 and 47 not changing the compositions.

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## Example 11

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[0095] In the sample 12 of the above Example 2, samples 12-1, 12-2, 12-3, 12-4, 12-5 and 12-6 coated with TiCN films having different orientation properties were prepared by changing coating temperatures and gas composition ratios in case of coating TiCN films. As to the obtained samples, results of evaluation of cutting performance are shown in Table 13.

[Table 13]

5	Sample	Crystal Plane Showing Maximum Peak Strength in X-Ray Diffraction	Wear Resistance	Chipping Resistance
			Cutting Condition 2	Cutting Condition 3
12-1		(111)	112min. 15sec.	5min. 17sec.
12-2		(422)	124min. 32sec.	5min. 25sec.
10	12-3	(311)	115min. 54sec.	5min. 12sec.
12-4		(220)	63min. 41sec.	4min. 36sec.
12-5		(420)	75min. 18sec.	4min. 49sec.
15	12-6	(331)	71min. 25sec.	4min. 21sec.

[0096] From the above results, it is understood that a coated hard metal having the maximum peak strength of X-ray diffraction on (111), (422) or (311) exhibits excellent cutting performance.

20 Example 12

[0097] Coating layers in a structure of TiN (0.5  $\mu\text{m}$ )/TiCN (3  $\mu\text{m}$ )/TiBN (0.5  $\mu\text{m}$ )/ZrO<sub>2</sub> (1  $\mu\text{m}$ )/Al<sub>2</sub>O<sub>3</sub> (15  $\mu\text{m}$ )/AlON (0.5  $\mu\text{m}$ )/TiCN (10  $\mu\text{m}$ ) were formed on the base materials 2 of the above Example 1 successively from inner layers. Film forming temperatures and gas composition ratios were varied in case of coating the TiCN films of the inner layers, to prepare samples 48-1, 48-2, 48-3, 48-4 and 48-5 forming TiCN films having different aspect ratios of crystal grains. Table 14 shows evaluation results of cutting performance.

[Table 14]

30	Sample	Aspect Ratio of Crystal Grain of Inner Layer TiN	Wear Resistance	Chipping Resistance
			Cutting Condition 1	Cutting Condition 3
48-1		3	5min. 15sec.	6min. 7sec.
48-2		7	8min. 21sec.	7min. 21sec.
35	48-3	15	10min. 34sec.	7min. 52sec.
48-4		26	9min. 27sec.	7min. 35sec.
48-5		42	6min. 18sec.	6min. 41sec.

[0098] From the above results, it is understood that samples 48-2, 48-3 and 48-4 in which the aspect ratios of the crystal grains are within the range of 5 to 30 in the TiCN films which are the thickest layers among the inner layers have excellent cutting performance.

40 Example 13

[0099] In the sample 17 of the above Example 3, the crystal grain diameters of Al<sub>2</sub>O<sub>3</sub> films were varied by changing film forming conditions (coating temperature and gas composition ratio), for preparing samples 17-1, 17-2, 17-3, 17-4 and 17-5 forming Al<sub>2</sub>O<sub>3</sub> films having different aspect ratios of crystal grains. Evaluation results of cutting performance are shown in Table 15.

[Table 15]

50	Sample	Aspect Ratio of Al <sub>2</sub> O <sub>3</sub> Crystal Grain	Wear Resistance	Chipping Resistance
			Cutting Condition	1 Cutting Condition 3
55	17-1	1	12min. 10sec.	5min. 41sec.
	17-2	3	12min. 3sec.	7min. 33sec.
	17-3	8	12min. 21sec.	8min. 5sec.

[Table 15] (continued)

Sample	Aspect Ratio of $\text{Al}_2\text{O}_3$ Crystal Grain	Wear Resistance	Chipping Resistance
		Cutting Condition	1 Cutting Condition 3
17-4	17	12min. 15sec.	7min. 21sec.
17-5	25	11min. 50sec.	6min. 3sec.

5 [0100] From the above results, it is understood that the tips of 17-2, 17-3 and 17-4 in which the aspect ratios of the crystal grains in the  $\text{Al}_2\text{O}_3$  films of the intermediate layers within the range of 3 to 20 have excellent cutting performance.

10 Example 14

15 [0101] In the sample 47 of the above Example 9, the crystal systems of  $\text{Al}_2\text{O}_3$  of intermediate layers were varied by changing the coating temperature and the gas composition ratio, for preparing two types of samples having different crystal systems. As to the obtained samples, evaluation results of cutting performance are shown in Table 16.

[Table 16]

Sample	Crystal System of $\text{Al}_2\text{O}_3$	Wear Resistance	Chipping Resistance
		Cutting Condition	2 Cutting Condition 3
47	mainly composed of $\kappa$	151min. 39sec.	7min. 24sec.
47-1	mainly composed of $\alpha$	162min. 15sec.	8min. 17sec.

20 [0102] From the above results, it is understood as to the crystal system of  $\text{Al}_2\text{O}_3$  of the intermediate layer that excellent cutting performance can be attained by being mainly composed of an  $\alpha$  type.

25 Example 15

30 [0103] In the tip of the sample 47-1 of Example 14, a sample 47-m in which only a portion of the intermediate layer of about  $1.0 \mu\text{m}$  in thickness being in contact with the inner layer and a portion of the intermediate layer of about  $1 \mu\text{m}$  in thickness being in contact with the outer layer were mainly composed of  $\kappa\text{-Al}_2\text{O}_3$  and a part of the intermediate layer held between the same was mainly composed of  $\alpha\text{-Al}_2\text{O}_3$  was prepared. The  $\text{Al}_2\text{O}_3$  intermediate layer having such a crystal system was prepared with raw material gas of  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{AlCl}_3$ . Formation of  $\kappa\text{-Al}_2\text{O}_3$  was performed under conditions of  $950^\circ\text{C}$ , 50 Torr and  $\text{CO}_2 = 2\%$ , and formation of  $\alpha\text{-Al}_2\text{O}_3$  was performed under conditions of  $1050^\circ\text{C}$ , 50 Torr and  $\text{CO}_2 = 5\%$ . Between the formation of the  $\kappa\text{-Al}_2\text{O}_3$  layer and the formation of the  $\alpha\text{-Al}_2\text{O}_3$  layer, the degree of vacuum was increased to not more than  $10^{-3}$  Torr. Results of employing a tip thus prepared and making evaluation as to wear resistance and chipping resistance are shown in Table 17.

[Table 17]

Sample	Crystal System of $\text{Al}_2\text{O}_3$	Wear Resistance	Chipping Resistance
		Cutting Condition 2	Cutting Condition 3
47-1	mainly composed of $\alpha$	162min. 15sec.	8min. 17sec.
47-m	mainly composed of $\kappa\text{-}\alpha\text{-}\kappa$	175min. 23sec.	8min. 31sec.

35 Example 16

40 [0104] In the sample 23 of Example 4, orientation properties of  $\text{Al}_2\text{O}_3$  films of intermediate layers were varied by controlling the coating temperatures and the gas composition ratios. As to obtained samples 23-1, 23-2, 23-3, 23-4 and 23-5, evaluation results of cutting performance are shown in Table 18.

[Table 18]

Sample	Crystal Plane Showing Maximum Peak Strength in X-Ray Diffraction	Wear Resistance	Chipping Resistance
		Cutting Condition 2	Cutting Condition 3
23-1	(104)	52min. 21sec.	8min. 4sec.
23-2	(116)	42min. 33sec.	7min. 52sec.
23-3	(113)	25min. 14sec.	7min. 15sec.
23-4	(024)	28min. 17sec.	6min. 59sec.
23-5	(300)	26min. 22sec.	7min. 3sec.

[0105] From the above results, it is understood that a coated hard metal in which an  $\text{Al}_2\text{O}_3$  film of an intermediate layer has the maximum peak strength of X-ray diffraction as to a crystal plane of (104) or (116) exhibits excellent cutting performance.

#### Example 17

[0106] Coating films in a structure of TiN (0.5  $\mu\text{m}$ )/TiCN (3  $\mu\text{m}$ )/TiBN (0.5  $\mu\text{m}$ )/ $\text{Al}_2\text{O}_3$  (15  $\mu\text{m}$ )/AlON (0.5  $\mu\text{m}$ )/TiCN (10  $\mu\text{m}$ ) were formed on the base materials 2 of Example 1 successively from inner layers. Film forming temperatures and gas composition ratios were changed, to vary the crystal grain sizes of TiCN of the inner layers,  $\text{Al}_2\text{O}_3$  of intermediate layers, and TiCN of outer layers. A sample 48-6 in which the aspect ratios of TiCN crystal grain sizes of the inner layer and the outer layer were larger than the aspect ratio of intermediate layer  $\text{Al}_2\text{O}_3$  crystal grains by at least twice, and a sample 48-7 of not more than twice were prepared. Distances between cracks in the coating layers by the crystal grains in these samples were measured by observing the same with an optical microscope after mirror-polishing sample sections. The distances between the cracks were obtained by performing 5 visual field measurement with the magnification of 500 times. The results are shown in Table 19. Also as to cutting performance of the obtained samples, results are shown in Table 19.

[Table 19]

Sample	Crack Distance of Inner Layer TiCN ( $\mu\text{m}$ )	Crack Distance of Outer Layer TiCN ( $\mu\text{m}$ )	Crack Distance of Intermediate Layer $\text{Al}_2\text{O}_3$ ( $\mu\text{m}$ )	Wear Resistance	Chipping Resistance
				Cutting Condition 1	Cutting Condition 3
48-6	80	70	100	12min. 45sec.	8min. 4sec.
48-7	100	100	100	10min. 11sec.	7min. 32sec.

[0107] From the above results, it is understood that a coated hard metal making crack distances of an inner layer and an outer layer smaller than crack distances of an intermediate layer in relation to crack distances of coating layers exhibits excellent cutting performance.

#### Example 18

[0108] In the samples 24 of Example 4, samples 24-1, 24-2 and 24-3 introducing substantially vertical cracks into coating layers by centrifugal-barrel after coating treatments were prepared. As to these samples, cutting performance is shown in Table 20.

[Table 20]

Sample	Crack Distance of Coating Layer ( $\mu\text{m}$ )	Wear Resistance	Chipping Resistance
		Cutting Condition 2	Cutting Condition 3
24	72	55min. 21sec.	6min. 39sec.

[Table 20] (continued)

Sample	Crack Distance of Coating Layer (μm)	Wear Resistance	Chipping Resistance
		Cutting Condition 2	Cutting Condition 3
24-1	38	59min. 42sec.	7min. 41sec.
24-2	25	63min. 17sec.	7min. 58sec.
24-3	16	56min. 3sec.	6min. 48sec.

[0109] By the above results, it is understood that a coated hard metal making crack distances of coating layers within the range of 20 to 40 μm has excellent cutting performance. The method of introducing cracks can be carried out by a method such as a treatment with a shot blast or an elastic grindstone, a quench treatment or the like, in place of the barrel treatment. These crack distances may not be formed on the overall coating layers, but a hard coated metal exhibiting excellent cutting performance is obtained when cracks are formed on a ridge portion of an insert at distances of this range.

#### Example 19

[0110] Hard layers shown in Table 21 were further coated on tip surfaces of the sample 31 of Example 5, to prepare tips of samples 31-1 to 31-5. These tips were employed for performing a cutting test by the cutting conditions 1 and 2 similarly to Example 1. Evaluation results are shown in Table 21.

[Table 21]

Sample	Structure of Hard Coating Layer	Wear Resistance	Chipping Resistance
		Cutting Condition 1	Cutting Condition 2
31	I of Table 1	4min. 57sec.	79min. 45sec.
31-1	I/Al <sub>2</sub> O <sub>3</sub> (2)/TiN(0.5)	6min. 39sec.	81min. 33sec.
31-2	I/TiBN(0.5)/Al <sub>2</sub> O <sub>3</sub> (1)	6min. 7sec.	84min. 16sec.
31-3	I/ZrO <sub>2</sub> (1)	5min 45sec.	82min. 51sec.
31-4	I/TiCN(0.5)/Al <sub>2</sub> O <sub>3</sub> <->	7min. 28sec.	78min. 27sec. (3)/TiN(0.5)
31-5	I/HfCN(0.5)HfO <sub>2</sub> (1)	6min. 54sec.	83min. 48sec.

[0111] As understood from the above results, it is understood that the samples further coating oxide thin films of Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub> etc. and/or TiN on the outer layers of TiCN are excellent in wear resistance in high-speed cutting in particular.

#### Example 20

[0112] As to the tip of the sample 44 of Example 8, samples 44-1, 44-2 and 44-3 in which coatings on ridge portions of inserts were partially ground/removed by an elastic grindstone were prepared. Average values of surface roughness Ra of the ground portions and cutting performance of the obtained samples are shown in Table 22.

[Table 22]

Sample	Average Value of Surface Roughness Ra in Removed Coating Portion (μm)	Wear Resistance	Chipping Resistance
		Cutting Condition	1 Cutting Condition 3
44	0.065	147min. 59sec.	7min. 29sec.
44-1	0.048	171min. 42sec.	8min. 5sec.
44-2	0.041	183min. 25sec.	8min. 34sec.
44-3	0.030	188min. 56sec.	8min. 21sec.

[0113] The average values of surface roughness Ra were measured by enlarging the insert ridge portions to 5000 times in ERA 8000 by ELIONIX INC. The average value of surface roughness Ra mentioned here is the average value of surface roughness Ra as to 180 horizontal lines of the measurement field. From the above results, it is understood that a coated hard metal in which the average value of surface roughness Ra of a coating on a ridge portion of an insert is not more than 0.05  $\mu\text{m}$  exhibits excellent cutting performance.

5 Example 21

[0114] ISO M20 cemented carbide (base material 1), ISO K20 (base material 2), and a commercially available cermet tool (base material 3) were prepared as base materials, and any of hard coating layers shown in Table 23 was formed on each base material by well-known chemical vapor deposition at a deposition temperature of 1000°C, for preparing tip-shaped tools of SNGN120408 respectively.

[Table 23]

15	Symbol	Structure of Hard Coating Layer (left side = base material side, inside parenthesis = film thickness( $\mu\text{m}$ ))
20	A'	TiN(0.5)/ZrO <sub>2</sub> (3)/TiCN(15)
25	B'	TiC(0.5)/TiCN(3)/TiBN(0.5)/ZrO <sub>2</sub> (1)/TiN(7)
30	C'	TiCN(2)/TiCO(0.5)/ZrO <sub>2</sub> (5)/TiCN(20)
	D'	TiN(0.5)/TiCNO(0.5)/ZrO <sub>2</sub> (18)/TiCN(30)/TiC(10)
	E'	ZrO <sub>2</sub> (3)/TiCN(15)
	F'	TiN(0.5)/ZrO <sub>2</sub> (0.3)/TiCN(15)
	G'	TiN(0.5)/TiCN(15)/ZrO <sub>2</sub> (3)
	H'	TiN(0.5)/ZrO <sub>2</sub> (3)
	I'	TiN(1)/TiBN(0.5)/ZrO <sub>2</sub> (3)/TiC(0.5)/TiCN(10)
	(Note) In relation to the structures of the hard coating layers in Table, the fact that the left sides are base material sides and the interiors of the parentheses indicate film thicknesses ( $\mu\text{m}$ ) also applies to the following Tables.	

[0115] The respective tips forming the hard coating layers on the base materials were employed for cutting work-pieces of SCM415 under cutting conditions of the following Table 24, and cutting performance was evaluated. The results are shown in Table 25, along with the combinations of the base materials and the hard coating layers.

[Table 24]

Cutting Condition	Cutting Speed (m/min)	Feed Rate (mm/rev)	Depth of Cut (mm)	Cutting Oil	Holder	Life Criterion
1	500	0.5	1.5	no	FN11R44A	$V_B=0.15\text{mm}$
2	200	0.4	1.5	yes	FN11R44A	$V_B=0.15\text{mm}$
3	100	0.3	1.5	no	FN11R44A	chipping

[Table 25]

Sample	Base Material	Coating Layer	Cutting Performance	
			Cutting Condition 1	Cutting Condition 2
1'	1	A'	5min. 27sec.	99min. 52sec.
2'	2	B'	3min. 41sec.	46min. 19sec.
3'	3	C'	9min. 33sec.	91min. 12sec.
4'	1	D'	17min. 26sec.	70min. 40sec.
5**	1	E'	separated in 38sec.	separated in 1min. 31sec.

[Table 25] (continued)

Sample	Base Material	Coating Layer	Cutting Performance	
			Cutting Condition 1	Cutting Condition 2
6"	1	F'	chipped in 59sec.	84min. 17sec.
7"	1	G'	chipped in 43sec.	17min. 10sec.
8"	1	H'	chipped in 25sec.	chipped in 1min. 24sec.

(Note) Samples provided with \* in Tables are comparative examples (and so forth).

[0116] From the above results, it is understood that the tips of the samples 1' to 4' of inventive Example exhibit excellent cutting performance not only in high-speed cutting (cutting conditions 1) but low-speed cutting (cutting conditions 2). By comparison of the samples 1' and 5', an effect of having a Ti compound as an inner layer is understood.

[0117] From comparison of the samples 1' and 6', it is understood that the effect is small if the film thickness of the  $ZrO_2$  intermediate layer is 0.3  $\mu m$ , while it is understood from comparison of the samples 1' and 7' that  $ZrO_2$  is superior in wear resistance when the same is employed as an intermediate layer rather than being coated as an outer layer. By comparison of the samples 1' and 8', it is understood that the Ti compound is superior in wear resistance to  $ZrO_2$  as an outer layer.

## Example 22

[0117] Hard coating layers shown in the following Table 26 were formed on the surfaces of the base materials 1 in the above Example 1, to prepare tips of samples 9' to 14'. These tips were employed for evaluating cutting performance by the cutting conditions 2 similarly to Example 21. As shown in Fig. 9, the workpiece 7 consisting of SCM435 having four grooves on its circumference was employed to test chipping resistance by the cutting conditions 3 of the above Table 25. The chipping resistance was evaluated by cutting times up to chipping of the tips. These results are shown in Table 26 together.

[Table 26]

Sample	Structure of Hard Coating Layer	Wear Resistance	Chipping Resistance
		Cutting Condition 2	Cutting Condition 3
9"	$ZrO_2(3)/TiCN(15)$	Separated in 1min. 49sec.	3min. 11sec.
10'	$TiC(0.2)/ZrO_2(3)/TiCN(15)$	67min. 45sec.	5min. 7sec.
11'	$TiC(0.5)/ZrO_2(3)/TiCN(15)$	91min. 27sec.	6min. 50sec.
12'	$TiC(3)/ZrO_2(3)/TiCN(15)$	113min. 21sec.	6min. 24sec.
13'	$TiC(5)/ZrO_2(3)/TiCN(15)$	97min. 14sec.	5min. 59sec.
14"	$TiC(10)/ZrO_2(3)/TiCN(15)$	88min. 5sec.	4min. 33sec.

[0118] As understood from the above results, the sample 9' having no Ti compound as an inner layer caused separation of the coating layers in an early stage in a wear resistance test since adhesion of the coating layers was low, and was of an extremely short life. The tip of the sample 14' exhibited a result slightly short of chipping resistance since the film thickness of the inner layer was large, while the same is excellent as to wear resistance. On the other hand, the samples 10' to 13' of inventive Example are excellent in wear resistance and chipping resistance, while the samples 11' and 12' are excellent in balance between wear resistance and chipping resistance in particular.

## Example 23

[0119] Hard coating layers shown in the following Table 27 were formed on surfaces of the base materials 2 in the above Example 21, to prepare tips of samples 15' to 21'. These tips were employed to evaluate cutting performance by the cutting conditions 1 similarly to Example 21. Further, chipping resistance was tested by the cutting conditions 3, similarly to Example 22. These results are shown in Table 27 together.

[Table 27]

Sample	Structure of Hard Coating Layer	Wear Resistance	Chipping Resistance
		Cutting Condition 1	Cutting Condition 3
15"	TiCN(2)/ZrO <sub>2</sub> (0.3)/TiC(13)	Chipped in 2min. 18sec.	7min. 19sec.
16'	TiCN(2)/ZrO <sub>2</sub> (0.5)/TiC(13)	8min. 22sec.	8min. 51sec.
17'	TiCN(2)/ZrO <sub>2</sub> (3)/TiC(13)	13min. 37sec.	9min. 25sec.
18'	TiCN(2)/ZrO <sub>2</sub> (10)/TiC(13)	15min. 41sec.	8min. 31sec.
19'	TiCN(2)/ZrO <sub>2</sub> (15)/TiC(13)	14min. 18sec.	8min. 17sec.
20'	TiCN(2)/ZrO <sub>2</sub> (20)/TiC(13)	12min. 34sec.	7min. 15sec.
21"	TiCN(2)/ZrO <sub>2</sub> (30)/TiC(13)	11min. 16sec.	6min. 8sec.

[0120] As understood from the above results, the samples other than the sample 15' having a small film thickness of the intermediate layer of ZrO<sub>2</sub> and the sample 21" having a large thickness exhibited cutting performance which is excellent in balance between wear resistance and chipping resistance, and the tips of the samples 17', 18' and 19' exhibited particularly excellent cutting performance above all.

#### Example 24

[0121] Hard coating layers shown in the following Table 28 were formed on the surfaces of the base materials 3 in Example 21, to prepare tips of samples 22' to 28'. These tips were employed to evaluate cutting performance by the cutting conditions 1 and 2 similarly to Example 21, and chipping resistance was tested by the cutting conditions 3 similarly to Example 22. These results are shown in Table 28 together.

[Table 28]

Sample	Structure of Hard Coating Layer	Wear Resistance	Wear Resistance	Chipping Resistance
		Cutting Condition 1	Cutting Condition 2	Cutting Condition 3
22"	TiN(4)/ZrO <sub>2</sub> (3)/TiCN(2)	chipped in 1min. 12sec.	chipped in 8min. 12sec.	9min. 47sec.
23'	TiN(4)/ZrO <sub>2</sub> (3)/TiCN(10)	4min. 15sec.	22min. 39sec	8min. 41sec.
24'	TiN(4)/ZrO <sub>2</sub> (3)/TiCN(15)	5min. 49sec.	53min. 10sec.	7min. 58sec.
25'	TiN(4)/ZrO <sub>2</sub> (3)/TiCN(30)	7min. 3sec.	85min. 14sec.	6min. 35sec.
26'	TiN(4)/ZrO <sub>2</sub> (3)/TiCN(46)	6min. 11sec.	72min. 51sec.	6min. 7sec.
27'	TiN(4)/ZrO <sub>2</sub> (3)/TiCN(95)	5min. 20sec.	65min. 32sec.	3min. 29sec.
28"	TiN(4)/ZrO <sub>2</sub> (3)/TiCN (120)	3min 5sec.	49min. 8sec.	2min. 36sec.

[0122] As understood from the above results, the samples other than the sample 22' and the sample 28" having small and large film thicknesses of outer layers of TiCN exhibited cutting performance which is excellent in balance between wear resistance and chipping resistance, and the tips of the samples 24', 25' and 26' exhibited particularly excellent cutting performance above all.

[0123] From the results of the above Example 23 shown in Table 27 and Example 24 shown in Table 28, it is understood that the samples 18' to 19' and 24' to 26' in which the total film thicknesses of the hard coating layers are in the range of 20 to 60  $\mu\text{m}$  are particularly excellent in balance between wear resistance and chipping resistance.

#### Example 25

[0124] Hard coating layers consisting of the structure of symbol I in the above Table 23 were formed on the surfaces of the base materials 1 in the above Example 21, to prepare tips of samples 29' to 34'. The shapes of crystal grains of the outermost TiCN layers in these samples were varied by changing film forming conditions. These tips were employed

to evaluate cutting performance by the cutting conditions 2 similarly to Example 21, and chipping resistance was tested by the cutting conditions 3 similarly to Example 22. These results are shown in Table 29 together.

[Table 29]

5	Sample	Aspect Ratio of TiCN Layer	Wear Resistance	Chipping Resistance
			Cutting Condition 2	Cutting Condition 3
10	29"	1.5	48min. 21sec.	4min. 9sec.
	30'	5	72min. 44sec.	6min. 11sec.
	31'	15	81min. 9sec.	7min. 59sec.
	32'	35	86min. 12sec.	9min. 5sec.
	33'	70	78min. 37sec.	8min. 21sec.
	34"	100	60min. 11sec.	8min. 5sec.

(Note) Samples provided with \* are comparative examples.

[0125] It is understood that the samples are excellent in wear resistance and chipping resistance when the aspect ratios of TiCN crystal grains forming the outermost TiCN layers among the outer coating layers are in the range of 5 to 80, and the samples 31' and 32' exhibit particularly excellent performance above all.

#### Example 26

[0126] When the C:N ratio of the TiCN layer which is the outer layer of the tip of the sample 1' (base material 1', hard coating layer A') prepared in the above Example 21 was calculated by obtaining the lattice constant by an X-ray diffraction method, it was 4:6 in molar ratio. Then, TiCN layers of different C:N ratios shown in Table 30 were formed as outer layers by varying the flow ratios of the raw material gas while inner layers and intermediate layers were identical to the sample 1', thereby preparing tips of samples 35' to 38'.

[0127] These tips were employed to evaluate cutting performance by the cutting conditions 1 and 2 similarly to Example 21, and chipping resistance was tested by the cutting conditions 3 similarly to Example 22. These results are shown in Table 30 together.

[Table 30]

35	Sample	C:N Ratio of TiCN Layer	Wear Resistance	Wear Resistance	Wear Resistance
			Cutting Condition 1	Cutting Condition 2	Cutting Condition 3
40	1'	4:6	5min. 27sec.	99min. 52sec.	5min. 59sec.
	35'	5:5	8min. 5sec.	127min. 24sec.	6min. 56sec.
	36'	6:4	9min. 17sec.	140min. 15sec.	6min. 28sec.
	37'	7:3	8min. 31sec.	157min. 18sec.	5min. 31sec.
	38'	8:2	7min. 42sec.	128min. 9sec.	4min. 20sec.

[0128] From the above results, it is understood that the tips of the samples 35' to 37' having the C:N ratios in the range of 5:5 to 7:3 in molar ratio are excellent in wear resistance and chipping resistance, and exhibit excellent cutting performance.

#### Example 27

[0129] In case of forming the hard coating layer of symbol D' in the above Table 23 on the surface of the base material 1, formation of the TiCN layer among the outer layer was performed by employing  $TiCl_4$  and  $CH_3CN$  as raw material gas and hydrogen gas as carrier gas at  $1000^\circ C$  and under pressure of 50 Torr, to prepare a tip of a sample 39'. Results of evaluating cutting performance with employment of the obtained tip by the cutting conditions 1 and 2 are shown in Table 31.

[0130] Table 31 also shows results of similar evaluation as to the sample 4' prepared by forming a TiCN layer by ordinary CVD similarly to the above except that  $TiCl_4$ ,  $CH_4$  and nitrogen gas were employed as raw material gas and

hydrogen gas was employed as carrier gas. From Table 31, it is understood that the sample 39' employing CH<sub>3</sub>CN as the raw material gas exhibits superior cutting performance.

[Table 31]

Sample	Wear Resistance	Wear Resistance
	Cutting Condition 1	Cutting Condition 2
4'	17min. 26sec.	70min. 40sec.
39'	28min. 15sec.	111min. 9sec.

## Example 28

[0131] In the tip of the sample 11' of the above Example 22, tips of samples 40' to 45' forming thin films consisting of TiBN, TiBNO, TiNO, TiCO, TiCNO or TiO<sub>2</sub> between intermediate layers of ZrO<sub>2</sub> and outer layers of TiCN by ordinary CVD at 1000°C in film thicknesses of about 0.5 μm were prepared. As to raw material gas, TiCl<sub>4</sub>, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub>, CO, NH<sub>3</sub> and BCl<sub>3</sub> were used in response to the film qualities. Results of evaluation of wear resistance and chipping resistance as to the obtained respective tips are shown in Table 32 in comparison with the tip of the sample 11'.

[Table 32]

Sample	Thin Film	Wear Resistance	Chipping Resistance
		Cutting Condition 2	Cutting Condition 3
11'	no	91min. 27sec.	6min. 50sec.
40'	TiBN	123min. 7sec.	7min. 24sec.
41'	TiBNO	115min. 43sec.	7min. 18sec.
42'	TiNO	112min. 14sec.	6min. 49sec.
43'	TiCO	128min. 51sec.	6min. 31sec.
44'	TiCNO	136min. 21sec.	7min. 6sec.
45'	TiO <sub>2</sub>	109min. 32sec	6min. 31sec.

[0132] From the results, it is understood that the samples 40' to 45' forming the thin films consisting of TiBN, TiBNO, TiNO, TiCO, TiCNO or TiO<sub>2</sub> between the intermediate layers of ZrO<sub>2</sub> and the outer layers of TiCN exhibit superior cutting performance to the sample 11' not provided with these thin films.

## Example 29

[0133] In the tip of the sample 25' of the above Example 24, tips of samples 46' to 51' forming thin films consisting of ZrC, ZrCN, ZrN, ZrCO, ZrCNO and ZrNO between intermediate layers of ZrO<sub>2</sub> and outer layers of TiCN by ordinary CVD at 1000°C in film thicknesses of about 0.5 μm were prepared. As to raw material gas, ZrCl<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub> were used in response to the film qualities. Results of evaluation of wear resistance and chipping resistance as to the obtained respective tips are shown in Table 33 in comparison with the tip of the sample 25'.

[Table 33]

Sample	Thin Film	Wear Resistance	Chipping Resistance
		Cutting Condition 2	Cutting Condition 3
25'	none	85min. 14sec.	6min. 35sec.
46'	ZrC	131min. 12sec.	7min. 19sec.
47'	ZrCN	138min. 41sec.	7min. 28sec.
48'	ZrN	125min. 33sec.	7min. 34sec.
49'	ZrCO	142min. 29sec.	7min. 9sec.

[Table 33] (continued)

Sample	Thin Film	Wear Resistance	Chipping Resistance
		Cutting Condition 2	Cutting Condition 3
50'	ZrCNO	135min. 8sec.	7min. 18sec.
51'	ZrNO	121min. 19sec.	7min. 47sec.

5 [0134] From the above results, it is understood that the samples 46' to 51' forming the thin films consisting of ZrC, ZrCN, ZrN, ZrCO, ZrCNO or ZrNO between the intermediate layers of  $ZrO_2$  and the outer layers of TiCN exhibit superior cutting performance to the sample 25' not provided with these thin films.

## Example 30

10 [0135] Samples 52' to 54' coating the intermediate layer of the tip of the sample 11' of the above Example 22 in replacement with  $Al_2O_3$  were prepared. These tips were employed to cut SUS304 under conditions of a cutting speed of 350 m/min., a feed rate of 0.5 mm/rev., and a depth of cut of 1.5 mm in a wet type for 20 minutes, for measuring amounts of plastic deformation and amounts of boundary wear. Chipping resistance under the cutting conditions of the above Table 24 was evaluated, and these results are shown in Table 34.

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[Table 34]

Sample	Intermediate Layer ( $\mu m$ )	Amount of Plastic Deformation (mm)	Amount of Boundary Wear (mm)	Chipping Resistance
				Cutting Condition 3
11'	$ZrO_2(3)$	0	0.13	6min. 50sec.
52'	$Al_2O_3(3)$	0.07	0.32	6min. 12sec.
53'	$Al_2O_3(10)$	0.02	0.35	5min. 53sec.
54'	$Al_2O_3(20)$	0	0.41	5min. 34sec.

(Note) The interiors of the parentheses indicate film thicknesses ( $\mu m$ ).

25 [0136] From these results, it is understood that the tip of the sample 11' coating  $ZrO_2$  as the intermediate layer is smaller in amount of boundary wear as compared with the tips of the remaining samples coating  $Al_2O_3$  as the intermediate layers, the amount of plastic deformation thereof is also smaller than the sample 52' of the same film thickness, and is excellent also in chipping resistance.

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## Example 31

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[0137] In the tip of the sample 25' of Example 24, layers whose compositions were continuously changed from  $ZrO_2$  to ZrN or from  $ZrO_2$  to ZrNO were formed between intermediate layers of  $ZrO_2$  and outer layers of TiCN in thicknesses of about 0.5  $\mu m$ . These layers were prepared by employing ordinary CVD, continuously changing temperatures from 900°C to 1000°C and continuously reducing raw material gas ratios of  $CO_2/N_2$ . Thus, samples 48'-c and 51'-c whose contents of O and N in the films were continuously changed were obtained. Results of evaluating wear resistance and chipping resistance by employing the obtained samples are shown in Table 35 in comparison with samples 48' and 51' whose compositions were not continuously changed.

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[Table 35]

Sample	Thin Film	Wear Resistance	Chipping Resistance
		Cutting Condition 2	Cutting Condition 3
48'	ZrN	125min. 33sec.	7min. 34sec.
51'	ZrNO	121min. 19sec.	7min. 47sec.
48'-c	$ZrO_2$ -ZrN	154min. 25sec.	8min. 16sec.
51'-c	$ZrO_2$ -ZrNO	150min. 13sec.	8min. 35sec.

[0138] From the above results, it is understood that the samples 48'-c and 51'-c continuously changing the compositions of the thin films exhibit further superior cutting performance as compared with the samples 48' and 51' whose compositions were not changed in the samples forming thin films consisting of ZrN or ZrNO between the intermediate layers of  $ZrO_2$  and the outer layers of TiCN.

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### Example 33

[0139] Hard layers shown in Table 36 were further coated on tip surfaces of the sample 31' of the above Example 25, to prepare tips of samples 31'-1 to 31'-5. These tips were employed for performing a cutting test by the cutting 10 conditions 1 and 2 similarly to Example 21. These evaluation results are shown in Table 36.

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[Table 36]

Sample	Structure of Hard Coating Layer	Wear Resistance	Wear Resistance
		Cutting Condition 1	Cutting Condition 2
31'	I' of Table 23	5min. 32sec.	81min. 9sec.
31'-1	I'/ $Al_2O_3$ (2)/TiN(0.5)	7min. 15sec.	83min. 14sec.
31'-2	I'/TiBN(0.5)/ $Al_2O_3$ (1)	6min. 49sec.	85min. 46sec.
31'-3	I'/ $ZrO_2$ (1)	7min. 5sec.	84min. 28sec.
31'-4	I'/TiCN(0.5)/ $Al_2O_3$ (3)/TiN(0.5)	7min. 38sec.	79min. 31sec.
31'-5	I'/HfCN(0.5)/ $HfO_2$ (1)	7min. 24sec.	82min. 17sec.

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[0140] As understood from the above results, it is understood that the samples 31'-1 to 5 further coating oxide thin films of  $Al_2O_3$ ,  $ZrO_2$  or  $HfO_2$  and/or TiN on the outer layers of TiCN are excellent in wear resistance in high-speed cutting in particular.

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### Industrial Availability

[0141] According to the present invention, it is possible to provide a coated hard metal having excellent wear resistance and chipping resistance. In particular, the present invention can provide a coated hard metal for a cutting tool which can sufficiently withstand employment not only in ordinary cutting conditions but in severe cutting conditions of a high speed or high efficiency under which the cutting edge temperature exceeds 1000°C.

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[0142] The embodiments disclosed this time must be regarded as illustrative in all points and not restrictive. The scope of the present invention is shown not by the above description but the scope of claims, and it is intended that all modifications in the meaning and scope which are equivalent to the scope of claims are included.

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### Claims

1. A coated hard metal material providing a hard coating layer on a surface of a base material selected from the group consisting of cemented carbide and cermet, wherein

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said hard coating layer comprises:

an inner layer being formed on said base material, and consisting essentially of at least one layer of a material selected from the group consisting of a carbide, a nitride, a carbo-nitride, a carbo-oxide, a carbonitrogen oxide and a boronitride of Ti,

an intermediate layer being formed on said inner layer, and mainly composed of an oxide selected from the group consisting of  $Al_2O_3$ ,  $ZrO_2$  and a mixture or a solid solution thereof, and

an outer layer being formed on said intermediate layer, and consisting essentially of at least one layer of a material selected from the group consisting of a carbide, a nitride, a carbo-nitride, a carbo-oxide, a carbonitrogen oxide and a boronitride of Ti,

the thickness of said inner layer is 0.1 to 5  $\mu m$ ,

the thickness of said intermediate layer is 5 to 50  $\mu m$  when the same is mainly composed of said  $Al_2O_3$ , and 0.5 to 20  $\mu m$  when the same is mainly composed of said  $ZrO_2$ ,

the thickness of said outer layer is 5 to 100  $\mu m$ , and

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wherein said outer layer includes a layer being mainly composed of columnar crystals having an aspect ratio of 5 to 80.

2. The coated hard metal material in accordance with claim 1, wherein said outer layer consists essentially of a layer being mainly composed of TiCN, and its C:N ratio is in the range of 5:5 to 7:3 in molar ratio.
3. The coated hard metal material in accordance with claim 2, further comprising a thin film being formed on said outer layer and consisting essentially of an oxide selected from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$ , and said thin film is thinner than said intermediate layer.
4. The coated hard metal material in accordance with claim 3, wherein TiCN of said outer layer has the maximum peak strength of X-ray diffraction as to a crystal plane selected from the group consisting of (111), (422) and (311).
5. The coated hard metal material in accordance with claim 4, wherein the thickest layer in said inner layer is mainly composed of columnar crystals having an aspect ratio of 5 to 30.
6. The coated hard metal material in accordance with claim 5, wherein said intermediate layer includes a layer being mainly composed of columnar crystals having an aspect ratio of 3 to 20.
7. The coated hard metal material in accordance with claim 1, wherein
  - the thickness of said inner layer is 0.5 to 3  $\mu\text{m}$ ,
  - the thickness of said intermediate layer is 10 to 40  $\mu\text{m}$  when the same is mainly composed of said  $\text{Al}_2\text{O}_3$ , and 3 to 15  $\mu\text{m}$  when the same is mainly composed of said  $\text{ZrO}_2$ ,
  - the thickness of said outer layer is 10 to 50  $\mu\text{m}$ , and
  - the total of the thicknesses of said inner layer, the intermediate layer and the outer layer is 25 to 60  $\mu\text{m}$  when said intermediate layer is mainly composed of  $\text{Al}_2\text{O}_3$ , and 20 to 60  $\mu\text{m}$  when said intermediate layer is mainly composed of  $\text{ZrO}_2$ .
8. The coated hard metal material in accordance with claim 7, further comprising an Al-containing thin film consisting essentially of a material selected from the group consisting of a nitride and an oxy-nitride of Al between said intermediate layer mainly composed of  $\text{Al}_2\text{O}_3$  and the outer layer in contact with said intermediate layer.
9. The coated hard metal material in accordance with claim 8, wherein the nitrogen content is reduced as said film approaches said intermediate layer and the oxygen content is increased as said film approaches said intermediate layer in said Al-containing thin film.
10. The coated hard metal material in accordance with claim 9, further comprising a thin film consisting essentially of a material selected from the group consisting of  $\text{TiBNO}$ ,  $\text{TiNO}$  and  $\text{TiO}_2$  between said Al-containing thin film and said outer layer.
11. The coated hard metal material in accordance with claim 1, further comprising a Zr-containing thin film consisting essentially of a material selected from the group consisting of a carbide, a nitride, a carbo-nitride, a carbo-oxide, an oxy-nitride and a carbonitrogen oxide of Zr between said intermediate layer mainly composed of  $\text{ZrO}_2$  and the outer layer in contact with said intermediate layer.
12. The coated hard metal material in accordance with claim 11, wherein the nitrogen content is reduced as said film approaches said intermediate layer and the oxygen content is increased as said film approaches said intermediate layer in said Zr-containing thin film.
13. The coated hard metal material in accordance with claim 12, further comprising a thin film consisting essentially of a material selected from the group consisting of  $\text{TiBNO}$ ,  $\text{TiNO}$  and  $\text{TiO}_2$  between said Zr-containing thin film and said outer layer.
14. The coated hard metal material in accordance with claim 1, wherein said intermediate layer is in contact with said outer layer through a thin film consisting essentially of a material selected from the group consisting of  $\text{TiBN}$ ,  $\text{TiCO}$  and  $\text{TiCNO}$ .

15. The coated hard metal material in accordance with claim 1, further comprising a thin film consisting essentially of a material selected from the group consisting of TiBNO, TiNO and TiO<sub>2</sub> between said intermediate layer and said outer layer in contact with said intermediate layer.

5 16. The coated hard metal material in accordance with claim 1 and 10 to 16, wherein Al<sub>2</sub>O<sub>3</sub> of said intermediate layer is mainly composed of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

10 17. The coated hard metal material in accordance with claim 16, wherein Al<sub>2</sub>O<sub>3</sub> of said intermediate layer has the maximum peak strength of x-ray diffraction as to a crystal plane selected from the group consisting of (104) and (116).

15 18. The coated hard metal material in accordance with claim 16, wherein the crystal system of Al<sub>2</sub>O<sub>3</sub> in said intermediate layer is mainly composed of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> around a portion being in contact with said inner layer and around a portion being in contact with said outer layer.

19. The coated hard metal material in accordance with claim 1, wherein said hard coating layer has a plurality of cracks, and the average of distances between adjacent cracks is 20 to 40  $\mu\text{m}$ .

20 20. The coated hard metal material in accordance with claim 1, wherein said hard coating layer has a plurality of cracks, and the distances between the cracks in said inner layer and said outer layer are smaller than the distances between the cracks in said intermediate layer.

25 21. The coated hard metal material in accordance with claim 1, having the shape of a cutting tool, and a part of said hard coating layer in a cutting edge of said cutting tool is removed so that a surface whose average value of surface roughness Ra is not more than 0.05  $\mu\text{m}$  is formed.

#### Patentansprüche

30 1. Ein beschichtetes Hartmetall-Material enthaltend eine harte Deckschicht auf der Oberfläche eines Grundmaterials ausgewählt aus der Gruppe bestehend aus zementiertem Carbid und Cermet, dadurch gekennzeichnet, daß die harte Deckschicht enthält:

35 eine innere Schicht, die auf dem Grundmaterial gebildet wird, und notwendigerweise aus mindestens einer Schicht aus einem Material ausgewählt aus der Gruppe bestehend aus einem Carbid, einem Nitrid, einem Carbonitrid, einem Carbo-Oxid, einem Carbostickstoffoxid und einem Bornitrid aus Titan,

40 eine Zwischenschicht, die auf der inneren Schicht gebildet wird, und hauptsächlich aus einem Oxid gebildet wird, aus der Gruppe bestehend aus Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> und einer Mischung oder einer festen Lösung davon, und einer äußeren Schicht, die auf der Zwischenschicht gebildet wird, bestehend notwendigerweise aus mindestens einer Schicht aus einem Material ausgewählt aus der Gruppe bestehend aus einem Carbid, einem Nitrid, einem Carbo-Oxid, einem Carbostickstoff-Oxid und einem Bornitrid aus Titan,

45 die Dicke der unteren Schicht beträgt 0,1 bis 5  $\mu\text{m}$ , die Dicke der Zwischenschicht beträgt 5 bis 50  $\mu\text{m}$ , wenn sie überwiegend aus Al<sub>2</sub>O<sub>3</sub> gebildet wird, und 0,5 bis 20  $\mu\text{m}$ , wenn diese hauptsächlich aus ZrO<sub>2</sub> gebildet wird, die Dicke der oberen Schicht beträgt 5 bis 100  $\mu\text{m}$ , und die obere Schicht enthält eine Schicht die hauptsächlich aus säulenartigen Kristallen gebildet wird, die ein Höhen-Breiten-Verhältnis von 5 bis 80 haben.

50 2. Ein beschichtetes Hartmetall-Material gemäß Anspruch 1, dadurch gekennzeichnet, daß die äußere Schicht notwendigerweise aus einer TiCN-Schicht gebildet wird, und in der das C : N -Verhältnis in einem Bereich von 5 : 5 bis 7 : 3 des molaren Verhältnisses liegt.

55 3. Ein beschichtetes Hartmetall-Material gemäß Anspruch 2 dadurch gekennzeichnet, daß weiterhin ein dünner Film enthalten ist, der auf der äußeren Schicht gebildet wird und notwendigerweise aus einem Oxid, ausgewählt aus der Gruppe bestehend aus Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> und HfO<sub>2</sub> besteht, und daß dieser dünne Film dünner ist als die Zwischenschicht.

4. Ein beschichtetes Hartmetall-Material gemäß Anspruch 3, **dadurch gekennzeichnet**, daß das TiCN der äußeren Schicht eine maximale Scheitelwertstärke der Röntgenbeugung in der Gitterebene hat, ausgewählt aus der Gruppe bestehend aus (111), (422) und (311).
5. Ein beschichtetes Hartmetall-Material gemäß Anspruch 4, **dadurch gekennzeichnet**, daß die dickste Schicht in der inneren Schicht hauptsächlich aus den säulenartigen Kristallen besteht, die ein Höhen-Breiten-Verhältnis von 5 bis 30 haben.
6. Ein beschichtetes Hartmetall-Material gemäß Anspruch 5, **dadurch gekennzeichnet**, daß die Zwischenschicht eine Schicht enthält, die notwendigerweise aus den säulenartigen Kristallen besteht, die ein Höhen-Breiten-Verhältnis von 3 bis 20 haben.
10. Ein beschichtetes Hartmetall-Material gemäß Anspruch 1, **dadurch gekennzeichnet**, daß die Dicke der inneren Schicht 0,5 bis 3 µm ist, die Dicke der Zwischenschicht 10 bis 40 µm ist, wenn sie überwiegend aus  $\text{Al}_2\text{O}_3$  gebildet wird, und 3 bis 15 µm, wenn diese hauptsächlich aus  $\text{ZrO}_2$  gebildet wird, die Dicke der äußeren Schicht beträgt 10 bis 50 µm, und die Gesamtdicke der inneren Schicht, der Zwischenschicht und der äußeren Schicht ist 25 bis 60 µm wenn die Zwischenschicht hauptsächlich aus  $\text{Al}_2\text{O}_3$ , und 20 bis 60 µm, wenn die Zwischenschicht hauptsächlich aus  $\text{ZrO}_2$  besteht.
15. Ein beschichtetes Hartmetall-Material gemäß Anspruch 7, **dadurch gekennzeichnet**, daß dieses weiterhin aus einem Al-enthaltenden dünnen Film, der zwischen der Zwischenschicht die hauptsächlich aus  $\text{Al}_2\text{O}_3$  gebildet wird, und der äußeren Schicht, die in Kontakt mit der Zwischenschicht ist liegt, und hauptsächlich aus einem Material ausgewählt ist aus der Gruppe bestehend aus einem Nitrid und einem Oxyd-Nitrid von Al besteht.
20. Ein beschichtetes Hartmetall-Material gemäß Anspruch 8, **dadurch gekennzeichnet**, daß der Stickstoffanteil in dem Al-enthaltenden dünnen Film zur Zwischenschicht hin abnimmt und der Sauerstoffanteil in diesem Film zur Zwischenschicht hin zunimmt.
25. Ein beschichtetes Hartmetall-Material gemäß Anspruch 9, **dadurch gekennzeichnet**, daß weiterhin ein dünner Film zwischen dem Al-enthaltenden dünnen Film und der äußeren Schicht enthalten ist, der im wesentlichen aus einem Material ist, ausgewählt aus der Gruppe bestehend aus  $\text{TiBNO}$ ,  $\text{TiNO}$  und  $\text{TiO}_2$ .
30. Ein beschichtetes Hartmetall-Material gemäß Anspruch 1, **dadurch gekennzeichnet**, daß weiterhin ein dünner Zr-enthaltender Film enthalten ist, der notwendigerweise aus einem Material ausgewählt aus der Gruppe bestehend aus einem Carbid, einem Nitrid, einem Carbo-Nitrid, einem Carbo-Oxid, einem Oxyd-Nitrid und einem Carbostickstoff-Oxid von Zr besteht, der zwischen der Zwischenschicht, die hauptsächlich aus  $\text{ZrO}_2$  gebildet wird, und der äußeren Schicht, die in Kontakt mit der Zwischenschicht ist, liegt.
35. Ein beschichtetes Hartmetall-Material gemäß Anspruch 11, **dadurch gekennzeichnet**, daß der Stickstoffanteil in dem Film zur Zwischenschicht hin abnimmt und der Sauerstoffanteil in diesem Zr-enthaltenden dünnen Film zur Zwischenschicht hin zunimmt.
40. Ein beschichtetes Hartmetall-Material gemäß Anspruch 12, **dadurch gekennzeichnet**, daß weiterhin ein dünner Film, der notwendigerweise aus einem Material ist, ausgewählt aus der Gruppe bestehend aus  $\text{TiBNO}$ ,  $\text{TiNO}$  und  $\text{TiO}_2$ , zwischen dem Zr-enthaltenden dünnen Film und der äußeren Schicht enthalten ist.
45. Ein beschichtetes Hartmetall-Material gemäß Anspruch 1, **dadurch gekennzeichnet**, daß die Zwischenschicht durch einen dünnen Film, der notwendigerweise aus einem Material ausgewählt aus der Gruppe bestehend aus  $\text{TiBN}$ ,  $\text{TiCO}$  und  $\text{TiCNO}$ , in Kontakt mit der äußeren Schicht ist.
50. Ein beschichtetes Hartmetall-Material gemäß Anspruch 1, **dadurch gekennzeichnet**, daß weiterhin ein dünner Film, der notwendigerweise aus einem Material ist, ausgewählt aus der Gruppe bestehend aus  $\text{TiBN}$ ,  $\text{TiNO}$  und  $\text{TiO}_2$ , zwischen der Zwischenschicht und der äußeren Schicht enthalten ist, und Kontakt mit der Zwischenschicht hat.
55. Ein beschichtetes Hartmetall-Material gemäß Anspruch 1 und 10 bis 16, **dadurch gekennzeichnet**, daß das  $\text{Al}_2\text{O}_3$  der Zwischenschicht hauptsächlich aus  $\alpha\text{-}\text{Al}_2\text{O}_3$  gebildet wird.

17. Ein beschichtetes Hartmetall-Material gemäß Anspruch 16, dadurch gekennzeichnet, daß das  $\text{Al}_2\text{O}_3$  der Zwischenschicht die maximale Scheitelwertstärke der Röntgenbeugung in der Gitterebene ausgewählt aus der Gruppe bestehend aus (104) und (116) hat.

5 18. Ein beschichtetes Hartmetall-Material gemäß Anspruch 16, dadurch gekennzeichnet, daß das Kristallsystem des  $\text{Al}_2\text{O}_3$  in der Zwischenschicht hauptsächlich aus  $\kappa\text{-}\text{Al}_2\text{O}_3$  gebildet wird, und mit einem Teil in Kontakt mit der inneren Schicht ist und mit einem Teil mit der äußeren Schicht in Kontakt ist.

10 19. Ein beschichtetes Hartmetall-Material gemäß Anspruch 1, dadurch gekennzeichnet, daß die beschichtete Hartschicht eine Vielzahl von Rissen aufweist, und der durchschnittliche Abstand zwischen den Rissen 20 bis 40  $\mu\text{m}$  ist.

15 20. Ein beschichtetes Hartmetall-Material gemäß Anspruch 1, dadurch gekennzeichnet, daß die beschichtete Hartschicht eine Vielzahl von Rissen hat, und die durchschnittlichen Abstände der Risse in der inneren Schicht und der äußeren Schicht kleiner sind als in der Zwischenschicht.

20 21. Ein beschichtetes Hartmetall-Material gemäß Anspruch 1, dadurch gekennzeichnet, daß es die Form eines Schneidewerkzeugs hat und ein Teil der harten Deckschicht in der Schneide des Schneidewerkzeugs entfernt wird, so daß eine Oberfläche gebildet wird, deren durchschnittlicher Wert für die Oberflächenrauhigkeit  $\text{Ra}$  nicht mehr als  $0,05 \mu\text{m}$  ist.

#### Revendications

25 1. Matériau métallique dur revêtu fournissant une couche de revêtement dur sur une surface d'un matériau de base choisi dans le groupe constitué par le carbure cémenté et le cermet, caractérisé en ce que ladite couche de revêtement dur comprend :

30 une couche interne étant formée sur ledit matériau de base, et consistant essentiellement en au moins une couche d'un matériau choisi dans le groupe constitué par un carbure, un nitride, un carbonitride, un carboxyde, un carboxynitride et un boronitride de Ti,

35 une couche intermédiaire étant formée sur ladite couche interne, et composée principalement d'un oxyde choisi dans le groupe constitué par  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  et un mélange ou une solution solide de ceux-ci, et une couche externe étant formée sur ladite couche intermédiaire, et consistant essentiellement en au moins une couche d'un matériau choisi dans le groupe constitué par un carbure, un nitride, un carbonitride, un carboxyde, un carboxynitride, et un boronitride de Ti,

40 l'épaisseur de ladite couche interne étant  $0,1$  à  $5 \mu\text{m}$ ,  
l'épaisseur de ladite couche intermédiaire étant  $5$  à  $50 \mu\text{m}$  quand celle-ci est composée principalement dudit  $\text{Al}_2\text{O}_3$ , et  $0,5$  à  $20 \mu\text{m}$  quand celle-ci est composée principalement dudit  $\text{ZrO}_2$ ,  
l'épaisseur de ladite couche externe étant  $5$  à  $100 \mu\text{m}$ , et

45 caractérisé en ce que ladite couche externe comprend une couche étant composée principalement de cristaux colonnaires ayant un rapport d'aspect de  $5$  à  $80$ .

50 2. Matériau métallique dur revêtu selon la revendication 1, caractérisé en ce que ladite couche externe consiste essentiellement en une couche étant composée principalement de  $\text{TiCN}$ , et son rapport  $\text{C} : \text{N}$  est dans la plage de  $5 : 5$  à  $7 : 3$  en rapport molaire.

55 3. Matériau métallique dur revêtu selon la revendication 2, comprenant en outre une pellicule mince formée sur ladite couche externe et consistant essentiellement en un oxyde choisi dans le groupe constitué par  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  et  $\text{HfO}_2$ , et ladite pellicule mince est plus mince que ladite couche intermédiaire.

60 4. Matériau métallique dur revêtu selon la revendication 3, caractérisé en ce que  $\text{TiCN}$  de ladite couche externe a une résistance de pic maximale par diffraction de rayons X sur un plan cristallin choisi dans le groupe constitué par (111), (422) et (311).

55 5. Matériau métallique dur revêtu selon la revendication 4, caractérisé en ce que la couche la plus épaisse dans ladite couche interne est composée principalement de cristaux colonnaires ayant un rapport d'aspect de  $5$  à  $30$ .

6. Matériau métallique dur revêtu selon la revendication 5, caractérisé en ce que ladite couche intermédiaire comprend une couche composée principalement de cristaux colonnaires ayant un rapport d'aspect de 3 à 20.

7. Matériau métallique dur revêtu selon la revendication 1, caractérisé en ce que

5 l'épaisseur de ladite couche interne est 0,5 à 3 µm,  
l'épaisseur de ladite couche intermédiaire est 10 à 40 µm quand celle-ci est composée principalement dudit  $Al_2O_3$ , et 3 à 15 µm quand celle-ci est composée principalement dudit  $ZrO_2$ ,  
l'épaisseur de ladite couche externe est 10 à 50 µm, et

10 le total des épaisseurs de ladite couche interne, de la couche intermédiaire et de la couche externe est 25 à 60 µm quand ladite couche intermédiaire est composée principalement de  $Al_2O_3$ , et 20 à 60 µm quand ladite couche intermédiaire est composée principalement de  $ZrO_2$ .

8. Matériau métallique dur revêtu selon la revendication 7, comprenant en outre une pellicule mince contenant Al constituée essentiellement d'un matériau choisi dans le groupe constitué par un nitride et un oxynitride de Al entre ladite couche intermédiaire composée principalement de  $Al_2O_3$  et la couche externe en contact avec ladite couche intermédiaire.

15 9. Matériau métallique dur revêtu selon la revendication 8, caractérisé en ce que la teneur en azote est réduite lorsque ladite pellicule s'approche de ladite couche intermédiaire et la teneur en oxygène est augmentée lorsque ladite pellicule s'approche de ladite couche intermédiaire dans ladite pellicule mince contenant Al.

20 10. Matériau métallique dur revêtu selon la revendication 9, comprenant en outre une pellicule mince constituée essentiellement d'un matériau choisi dans le groupe constitué par TiBNO, TiNO et  $TiO_2$  entre ladite pellicule mince contenant Al et ladite couche externe.

25 11. Matériau métallique dur revêtu selon la revendication 1, comprenant en outre une pellicule mince contenant Zr constituée essentiellement d'un matériau choisi dans le groupe constitué par un carbure, un nitride, un carbonitride, un carboxyde, un oxynitride et un carboxynitride de Zr entre ladite couche intermédiaire composée principalement de  $ZrO_2$  et la couche externe en contact avec ladite couche intermédiaire.

30 12. Matériau métallique dur revêtu selon la revendication 11, caractérisé en ce que la teneur en azote est réduite quand ladite pellicule s'approche de ladite couche intermédiaire et la teneur en oxygène augmente quand ladite pellicule s'approche de ladite couche intermédiaire dans ladite pellicule mince contenant Zr.

35 13. Matériau métallique dur revêtu selon la revendication 12, comprenant en outre une pellicule mince constituée essentiellement d'un matériau choisi dans le groupe constitué par TiBNO, TiNO et  $TiO_2$  entre ladite pellicule mince contenant Zr et ladite couche externe.

40 14. Matériau métallique dur revêtu selon la revendication 1, caractérisé en ce que ladite couche intermédiaire est en contact avec ladite couche externe à travers une pellicule mince constituée essentiellement d'un matériau choisi dans le groupe constitué par TiBN, TiCO et TiCNO.

45 15. Matériau métallique dur revêtu selon la revendication 1, comprenant en outre une pellicule mince constituée essentiellement d'un matériau choisi dans le groupe constitué par TiBNO, TiNO et  $TiO_2$  entre ladite couche intermédiaire et ladite couche externe en contact avec ladite couche intermédiaire.

50 16. Matériau métallique dur revêtu selon les revendications 1 et 10 à 16, caractérisé en ce que  $Al_2O_3$  de ladite couche intermédiaire est composé principalement de  $\alpha$ - $Al_2O_3$ .

17. Matériau métallique dur revêtu selon la revendication 16, caractérisé en ce que  $Al_2O_3$  de ladite couche intermédiaire a la résistance de pic maximale à la diffraction par rayons X sur un plan cristallin choisi dans le groupe constitué de (104) et (116).

55 18. Matériau métallique dur revêtu selon la revendication 16, caractérisé en ce que le système cristallin de  $Al_2O_3$  dans ladite couche intermédiaire est composé principalement de  $\kappa$ - $Al_2O_3$  autour d'une partie étant en contact avec ladite couche interne et autour d'une partie étant en contact avec ladite couche externe.

19. Matériau métallique dur revêtu selon la revendication 1, caractérisé en ce que ladite couche de revêtement dur a une pluralité de craquelures, et la moyenne des distances entre les craquelures adjacentes est 20 à 40 µm.

5 20. Matériau métallique dur revêtu selon la revendication 1, caractérisé en ce que ladite couche de revêtement dur a une pluralité de craquelures, et les distances entre les craquelures dans ladite couche interne et dans ladite couche externe sont inférieures aux distances entre les craquelures dans ladite couche intermédiaire.

10 21. Matériau métallique dur revêtu selon la revendication 1, ayant la forme d'un outil de coupe, et une partie de ladite couche de revêtement dur dans un bord de coupe dudit outil de coupe est éliminée de manière que soit formée une surface dont la valeur moyenne de rugosité de surface Ra n'est pas supérieure à 0,05 µm.

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FIG. 1

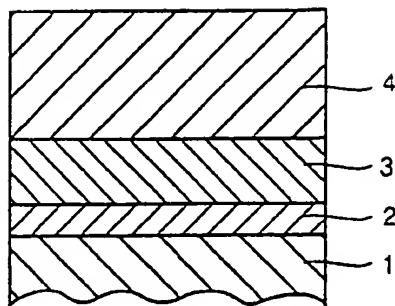


FIG. 2A

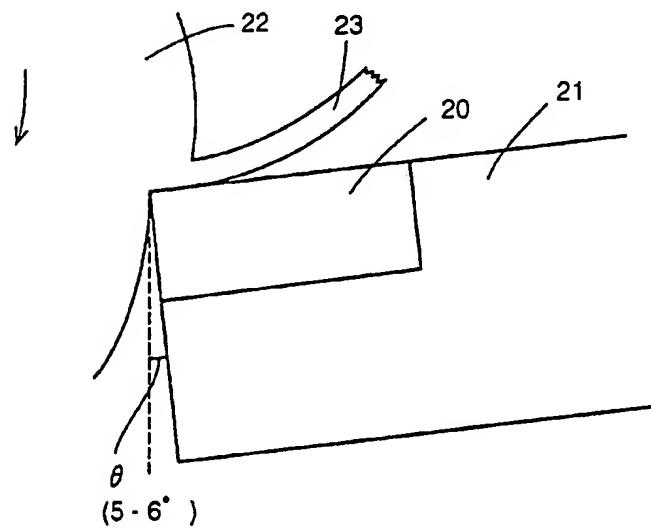


FIG. 2B

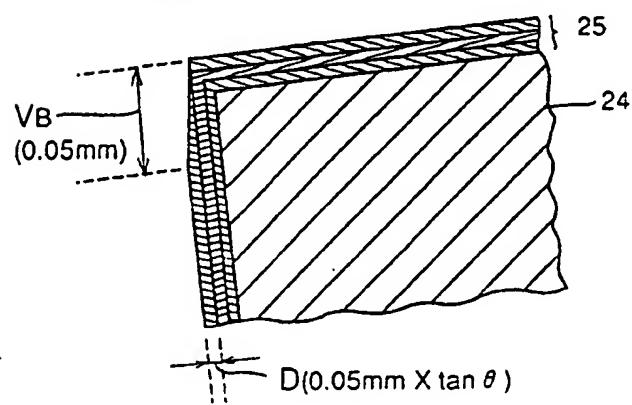


FIG. 3

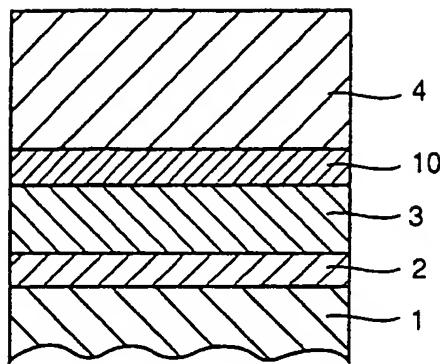


FIG. 4

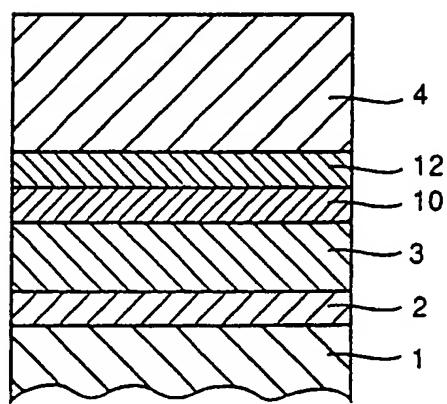


FIG. 5

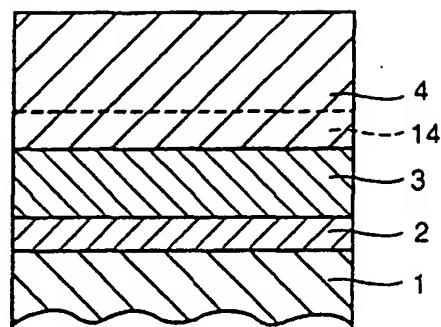


FIG. 6

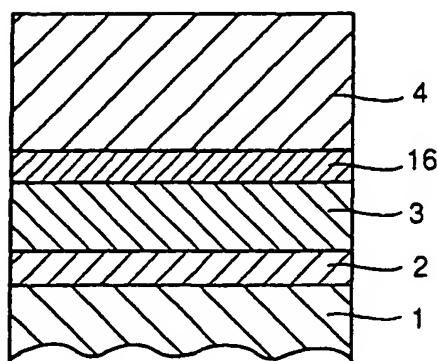


FIG. 7

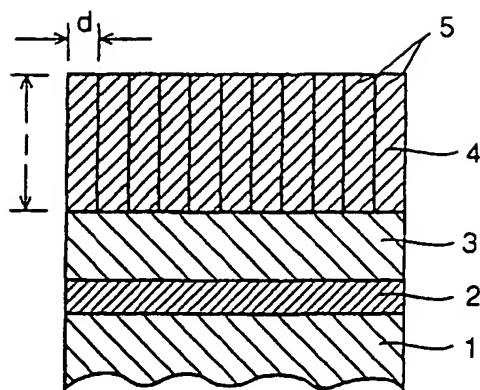


FIG. 8

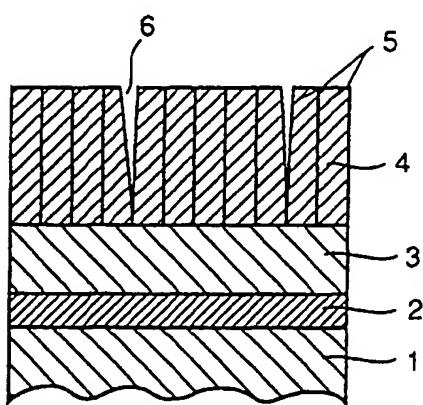


FIG. 9

